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ABSTRACT

This training manual presents material on the theoretical concepts involved in the methods listed in the Federal Register as approved for determination of trace metals. Emphasis is on laboratory operations. This course is intended for chemists and technicians with little or no experience in analytical methods for trace metals. Students should have basic laboratory skills including use of volumetric glassware and titration assemblies. Topics include sample handling, atomic absorption, spectrophotometry, flame photometry, and techniques for determining various trace metals. (CO)

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United States
Environmental Protection
Agency

National Training
and Operational
Technology Center
Cincinnati OH 45268

EPA-430/1-79-006
July 1979

Water

Analytical Methods for Trace Metals

Training Manual

ED209118

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Analytical Methods for Trace Metals

This course is for chemists and technicians with little or no experience in analytical methods for trace metals. Applicants should have basic laboratory skills including use of volumetric glassware and titration assemblies.

After successfully completing the course, the student will have knowledge about the theoretical concepts involved in the methods listed in the Federal Register as approved for determining concentrations of trace metals, and will be able to use these methods in a laboratory.

The training consists of classroom instruction, student performance of laboratory procedures, and discussion of each laboratory assignment and reported results.

U. S. ENVIRONMENTAL PROTECTION AGENCY
Office of Water Program Operations
National Training and Operational Technology Center

DISCLAIMER

Reference to commercial products, trade names or manufacturers is for purposes of example and illustration. Such references do not constitute endorsement by the Office of Water Program Operations, U. S. Environmental Protection Agency.

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FEDERAL REGISTER GUIDELINES FOR CHEMICAL ANALYSES

I FEDERAL REGISTER GUIDELINES

A Authority

1 In 1972, section 304(g) of Public Law 92-500, required the EPA Administrator to promulgate guidelines establishing test procedures for the analysis of pollutants that would include the factors that must be provided in any state certification (section 401), or National Pollutant Discharge Elimination System (NPDES) permit application (section 402).

2 These test procedures are to be used by applicants to demonstrate that effluent discharges meet applicable pollutant discharge limitations, and by the states and other enforcers in routine or random monitoring of effluents to verify effectiveness of pollution control measures.

B Establishment

Following a proposed listing there was a period for reply by interested parties. The first rulemaking was published in the Federal Register on October 16 1973.[1]

C Current Guidelines

Proposed amendments and update were published in 1975. The current guidelines were issued in the December 1, 1976[2] Federal Register.

D Format

The "Approved Test Procedures" are given in a table which lists 115 parameters, the methodology to be used to determine them and either the page number in standard references or else a source where the analytical procedure can be found.

1 Divisions

The parameters are listed alphabetically including four subcategories of related tests:

a bacteria

b metals

c radiological

d residue

2 Standard References

Those cited most often as sources of analytical procedures for the listings are the EPA Chemical Methods Manual,[3] Standard Methods,[4] ASTM[5] and U.S. Geological Survey.[6] Other sources of procedures are given in footnotes to the Table.

II EPA CHEMICAL METHODS MANUAL

A Analytical Procedures

The EPA Chemical Methods Manual was developed for their water quality laboratories, using Standard Methods and ASTM as basic references. In many cases, EPA modified methods from these sources or else developed methods suitable for their own laboratories.

B Sampling and Preservation Techniques

The manual also contains a section on sampling and preservation. This is in tabular form and contains information on volumes required for analysis, the type of container that can be used, preservation measures and holding times. The current Federal Register references this Table for recommendations on these aspects of sample handling for NPDES/Certification purposes.

C Precision and Accuracy Data

Precision and accuracy data from inter-laboratory quality control studies are given for most of the methods cited.

III METHODS NOT IN 1976 GUIDELINES

A Application to Use

A system has been established for permit holders to apply for approval to use methods not listed in the December 1, 1976 Federal Register. One supplies reasons for using an alternative method to the EPA Regional Administrator through the state agency which issues certifications and/or permits. If the state does not have such an agency, the application is submitted directly to the EPA Regional Administrator.

B Order of Processing

Before approving such applications, the Regional Administrator sends a copy to the Director of the EPA Environmental Monitoring and Support Laboratory (EMSL) for review and recommendation. If the Regional Administrator rejects any application, a copy is also sent to EMSL. Within 90 days the applicant is to be notified (along with the appropriate state agency) of approval or rejection. EMSL also receives a copy of approval or rejection notifications for purposes of national coordination.

IV REQUIRED ANALYSES

Which measurements are to be done and reported depend on the specifications of the individual certifications or permits.

A Mandatory for Secondary Plants

By July 1, 1977 all municipal secondary wastewater treatment plants will be required to measure and report pH, BOD_5 (biochemical oxygen demand), suspended solids and flow. Many plants are required to report these now.

B Additional for Secondary Plants

Measurements which also may be required of secondary treatment plants are fecal coliform bacteria, residual chlorine, settleable solids, COD (chemical oxygen demand), total phosphorus, and the nitrogen series (total Kjeldahl N, NH_3-N, NO_3-N, NO_2-N).

C Municipalities and Industries

Other required analyses depend on local factors for a municipality. Each industry has requirements pertinent to the processes involved.

1 Non-specific

Non-specific measurements to assess overall water quality might be required like acidity, alkalinity, color, turbidity, specific conductance.

2 Organics

Various organic analyses might be relevant such as total organic carbon, organic nitrogen, phenols, oil and grease, surfactants, pesticides.

3 Metals

Specified metals may be of interest. Currently, the Federal Register lists 35 trace metals in the test procedure guidelines.

4 Others

Cyanide, bromide, chloride, fluoride and hardness are other measurements that might be required.

V METHODOLOGY AND SKILLS

A Methodology

The analytical methods specified in the Federal Register for these measurements range from "wet" procedures using equipment commonly found in most laboratories, to procedures requiring sophisticated instruments such as an organic carbon analyzer or an atomic absorption unit.

B Skills

The degree of analytical skills required to perform the analyses likewise varies, as does the cost of having such analyses performed by service laboratories.

VI OTHER ANALYTICAL CONSIDERATIONS

A Sample

The importance of securing a representative sample of the type (grab or composite) specified by the permit cannot be over-stressed.

B Record Keeping

Keeping complete and permanent records about the sample is also essential. Such records include conditions when the sample was collected, chain of custody signatures and details and results of analyses.

C Quality Control

Whether the analyses are done in-house or by a service laboratory, an Analytical Quality Control Program should be established. Fifteen to twenty percent of analytical time (cost) should be given to checking standard curves for colorimetry, analyzing duplicate samples to check precision and analyzing spiked samples to check accuracy. Recording precision and accuracy data on quality control charts is an effective method of using such data as a daily check on analytical performance. This can also be done with numbers reported on "blind" samples sent to service labs.

VII SUMMARY

The December 1, 1976 Federal Register promulgates guidelines establishing test procedures for the analysis of pollutants which might be required for certification (PL 92-500, section 401) or for NPDES permits (PL 92-500, section 402). The issue lists page numbers in standard references where procedures can be found to measure the 115 parameters listed. It also updates the regulations for application to use methods not cited in the guidelines. The measurements which must be made are specified by either a state agency or by U. S. EPA. Apparatus and professional skills to do the measurements will vary. Representative samples, complete records and analytical quality control measures are all necessary elements for producing reliable data.

REFERENCES

1 Federal Register, Vol 38, No 199, Tuesday, October 16, 1973, Title 40, Chapter 1, Subchapter D, Part 136, page 28758.

2 Federal Register, Vol 41, No. 232, Wednesday, December 1, 1976, Title 40, Chapter 1, Subchapter D, Part 136, page 52780.

3 Methods for Chemical Analyses of Water and Wastes, 1974, EPA, EMSL, Cincinnati, Ohio.

4 Standard Methods for the Examination of Water and Wastewater, 14th ed., 1976, APHA, Washington, D. C.

5 Annual Book of Standards, Part 31, Water, 1975, ASTM, Philadelphia, Pennsylvania.

6 Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases, U.S.G.S. Survey Techniques of Water - Resources Inventory, Book 5, Chapter A1, 1970, U.S. GPO, Washington, D. C.

This outline was prepared by A. D. Kroner, Chemist, National Training and Operational Technology Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268

Descriptors: Chemical analysis, chemical guidelines, self-monitoring requirements, non-approved analytical methods, NPDES

METHODOLOGY FOR CHEMICAL ANALYSIS OF WATER AND WASTEWATER

I INTRODUCTION

This outline deals with chemical methods which are commonly performed in water quality laboratories. Although a large number of constituents or properties may be of interest to the analyst, many of the methods employed to measure them are based on the same analytical principles. The purpose of this outline is to acquaint you with the principles involved in commonly-used chemical methods to determine water quality.

II PRE-TREATMENTS

For some parameters, a preliminary treatment is required before the analysis begins. These treatments serve various purposes.

A Distillation - To isolate the constituent by heating a portion of the sample mixture to separate the more volatile part(s), and then cooling and condensing the resulting vapor(s) to recover the volatilized portion.

B Extraction - To isolate/concentrate the constituent by shaking a portion of the sample mixture with an immiscible solvent in which the constituent is much more soluble.

C Filtration - To separate undissolved matter from a sample mixture by passing a portion of it through a filter of specified size. Particles that are dissolved in the original mixture are so small that they stay in the sample solution and pass through the filter.

D Digestion - To change constituents to a form amenable to the specified test by heating a portion of the sample mixture with chemicals.

III METERS

For some parameters, meters have been designed to measure that specific constituent or property.

A pH Meters

pH (hydrogen ion concentration) is measured as a difference in potential across a glass membrane which is in contact with the sample and with a reference solution. The sensor apparatus might be combined into one probe or else it is divided into an indicating electrode (for the sample) and a reference electrode (for the reference solution). Before using, the meter must be calibrated with a solution of known pH (a buffer) and then checked for proper operation with a buffer of a different pH value.

B Dissolved Oxygen Meters

Dissolved oxygen meters measure the production of a current which is proportional to the amount of oxygen gas reduced at a cathode in the apparatus. The oxygen gas enters the electrode through a membrane, and an electrolyte solution or gel acts as a transfer and reaction media. Prior to use the meter must be calibrated against a known oxygen gas concentration.

C Conductivity Meters

Specific conductance is measured with a meter containing a Wheatstone bridge which measures the resistance of the sample solution to the transmission of an electric current. The meter and cell are calibrated according to the conductance of a standard solution of potassium chloride at 25°C, measured by a "standard" cell with electrodes one cm square spaced one cm apart. This is why results are called "specific" conductance.

D Turbidimeters

A turbidimeter compares the intensity of light scattered by particles in the sample under defined conditions with the intensity of light scattered by a standard reference suspension.

IV SPECIFIC ION ELECTRODES

Just as the conventional glass electrode for pH develops an electrical potential in response to the activity of hydrogen ion in solution, the specific ion electrode develops an electrical potential in response to the activity of the ion for which the electrode is specific. The potential and activity are related according to the Nernst equation. Simple analytical techniques can be applied to convert activity to an expression of concentration.

These electrodes are used with a pH meter with an expanded mV scale or with a specific ion meter. Two examples are the ammonia and fluoride electrodes.

A Ammonia

The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.

B Fluoride

The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions. The cell may be represented by Ag/Ag Cl, Cl^-(0.3), F^-(0.001) LaF/test solution/SCE/. It is used in conjunction with a standard single junction reference electrode.

V GENERAL ANALYTICAL METHODS

A Volumetric Analysis

Titrations involve using a buret to measure the volume of a standard solution of a substance required to completely react with the constituent of interest in a measured volume of sample. One can then calculate the original concentration of the constituent of interest.

There are various ways to detect the end point when the reaction is complete.

1 Color change indicators

The method may utilize an indicator which changes color when the reaction is complete. For example, in the Chemical Oxygen Demand Test the indicator, ferroin, gives a blue-green color to the mixture until the oxidation-reduction reaction is complete. Then the mixture is reddish-brown.

Several of these color-change titrations make use of the iodometric process whereby the constituent of interest quantitatively releases free iodine. Starch is added to give a blue color until enough reducing agent (sodium thiosulfate or phenylarsine oxide) is added to react with all the iodine. At this end point, the mixture becomes colorless.

2 Electrical property indicators

Another way to detect end points is a change in an electrical property of the solution when the reaction is complete. In the chlorine titration a cell containing potassium chloride will produce a small direct current as long as free chlorine is present. As a reducing agent (phenylarsine oxide) is added to reduce the chlorine, the microammeter which measures the existing direct current registers a lower reading on a scale. By observing the scale, the end point of total reduction of chlorine can be determined because the direct current ceases.

3 Specified end points

For acidity and alkalinity titrations, the end points are specified pH values for the final mixture. The pH values are those existing when common acidity or alkalinity components have been neutralized. Thus acidity is determined by titrating the sample with a standard alkali to pH 8.2 when carbonic acid would be neutralized to $(CO_3)^=$. Alkalinity (except for highly acidic samples) is determined by titrating the sample with a standard acid to pH 4.5 when the carbonate present has been converted to carbonic acid. pH meters are used to detect the specified end points.

B Gravimetric Procedures

Gravimetric methods involve direct weighing of the constituent in a container. An empty container is weighed, the constituent is separated from the sample mixture and isolated in the container, then the container with the constituent is weighed. The difference in the weights of the container before and after containing the constituent represents the weight of the constituent.

The type of container depends on the method used to separate the constituent from the sample mixture. In the solids determinations, the container is an evaporating dish (total or dissolved) or a glass fiber filter disc in a crucible (suspended). For oil and grease, the container is a flask containing a residue after evaporation of a solvent.

C Combustion

Combustion means to add oxygen. In the Total Organic Carbon Analysis, combustion is used within an instrument to convert carbonaceous material to carbon dioxide. An infrared analyzer measures the carbon dioxide.

VI PHOTOMETRIC METHODS

These methods involve the measurement of light that is absorbed or transmitted quantitatively either by the constituent of interest or else by a substance containing the constituent of interest which has resulted from some treatment of the sample. The quantitative aspect of these photometric methods is based on applying the Lambert-Beer Law which established that the amount of light absorbed is quantitatively related to the concentration of the absorbing medium at a given wavelength and a given thickness of the medium through which the light passes.

Each method requires preparing a set of standard solutions containing known amounts of the constituent of interest. Photometric values are obtained for the standards. These are used to draw a calibration (standard) curve by plotting photometric values against the concentrations. Then, by locating the photometric value for the sample on this standard curve, the unknown concentration in the sample can be determined.

A Atomic Absorption

Atomic Absorption (AA) instruments utilize absorption of light of a characteristic wavelength. This form of analysis involves aspirating solutions of metal ions (cations) or molecules containing metals into a flame where they are reduced to individual atoms in a ground electrical state. In this condition, the atoms can absorb radiation of a wavelength characteristic for each element. A lamp containing the element of interest as the cathode is used as a source to emit the characteristic line spectrum for the element to be determined.

The amount of energy absorbed is directly related to the concentration of the element of interest. Thus the Lambert-Beer Law applies. Standards can be prepared and tested and the resulting absorbance values can be used to construct a calibration (standard) curve. Then the absorbance value for the sample is located on this curve to determine the corresponding concentration.

Once the instrument is adjusted to give optimum readings for the element of interest, the testing of each solution can be done in a matter of seconds. Many laboratories wire recorders into their instruments to rapidly transcribe the data, thus conserving time spent on this aspect of the analysis. Atomic absorption techniques are generally used for metals and semi-metals in solution or else solubilized through some form of sample processing. For mercury, the principle is utilized but the absorption of light occurs in a flameless situation with the mercury in the vapor state and contained in a closed glass cell.

B Flame Emission

Flame emission photometry involves measuring the amount of light given off by atoms drawn into a flame. At certain temperatures, the flame raises the electrons in atoms to a higher energy level. When the electrons fall back to a lower energy level, the atoms lose (emit) radiant energy which can be detected and measured.

Again standards must be prepared and tested to prepare a calibration (standard) curve. Then the transmission value of the sample can be located on the curve to determine its concentration.
Many atomic absorption instruments can be used for flame emission photometry. Sodium and potassium are very effectively determined by the emission technique.

However, for many elements, absorption analysis is more sensitive because there are a great number of unexcited atoms in the flame which are available to absorb the radiant energy.

C Colorimetry

Colorimetric analyses involve treating standards which contain known concentrations of the constituent of interest and also the sample with reagents to produce a colored solution. The greater the concentration of the constituent, the more intense will be the resulting color.

The Lambert-Beer Law which relates the absorption of light to the thickness and concentration of the absorbing medium applies. Accordingly, a spectrophotometer is used to measure the amount of light of appropriate wavelength which is absorbed by the same thickness of each solution. The results from the standards are used to construct a calibration (standard) curve. Then the absorbance value for the sample is located on this curve to determine the corresponding concentration.

Many of the metals and several other parameters (phosphorus, ammonia, nitrate, nitrite, etc.) are determined in this manner.

VII GAS-LIQUID CHROMATOGRAPHY

Chromatography techniques involve a separation of the components in a mixture by using a difference in the physical properties of the components. Gas-Liquid Chromatography (GLC) involves separation based on a difference in the properties of volatility and solubility. The method is used to determine algicides, chlorinated organic compounds and pesticides.

The sample is introduced into an injector block which is at a high temperature (e.g. 210°C), causing the liquid sample to volatilize. An inert carrier gas transports the sample components through a liquid held in place as a thin film on an inert solid support material in a column.
Sample components pass through the column at a speed partly governed by the relative solubility of each in the stationary liquid. Thus the least soluble components are the first to reach the detector. The type of detector used depends on the class of compounds involved. All detectors function to sense and measure the quantity of each sample component as it comes off the column. The detector signals a recorder system which registers a response.

As with other instrumental methods, standards with known concentrations of the substance of interest are measured on the instrument. A calibration (standard) curve can be developed and the concentration in a sample can be determined from this graph.

Gas-liquid chromatography methods are very sensitive (nanogram, picogram quantities) so only small amounts of samples are required. On the other hand, this extreme sensitivity often necessitates extensive clean-up of samples prior to GLC analysis.

VIII AUTOMATED METHODS

The increasing number of samples and measurements to be made in water quality laboratories has stimulated efforts to automate these analyses. Using smaller amounts of sample (semi-micro techniques), combining reagents for fewer measurements per analysis, and using automatic dispensers are all means of saving analytical time.

However, the term "automated laboratory procedures" usually means automatic introduction of the sample into the instrument, automatic treatment of the sample to test for a component of interest, automatic recording of data and, increasingly, automatic calculating and print-out of data. Maximum automation systems involve continuous sampling direct from the source (e.g. an in-place probe) with telemetering of results to a central computer.

Automated methods, especially those based on colorimetric methodology, are recognized for several water quality parameters including alkalinity, ammonia, nitrate, nitrite, phosphorus, and hardness.

IX SOURCES OF PROCEDURES

Details of the procedure for an individual measurement can be found in reference books. There are three particularly-recognized books of procedures for water quality measurements.

A Standard Methods[1]

The American Public Health Association, the American Water Works Association and the Water Pollution Control Federation prepare and publish "Standard Methods for the Examination of Water and Wastewater."

As indicated by the list of publishers, this book contains methods developed for use by those interested in water or wastewater treatment.

B ASTM Standards[2]

The American Society for Testing and Materials publishes an "Annual Book of ASTM Standards" containing specifications and methods for testing materials. The "book" currently consists of 47 parts.

The part applicable to water was formerly Part 23. It is now Part 31, Water.

The methods are chosen by approval of the membership of ASTM and are intended to aid industry, government agencies and the general public. Methods are applicable to industrial waste waters as well as to other types of water samples.

C EPA Methods Manual[3]

The United States Environmental Protection Agency publishes a manual of "Methods for Chemical Analysis of Water and Wastes."

EPA developed this manual to provide methodology for monitoring the quality of our Nation's waters and to determine the impact of waste discharges. The test procedures were carefully selected to meet these needs, using Standard Methods and ASTM as basic references. In many cases, the EPA manual contains completely described procedures because they modified methods from the basic references. Otherwise, the manual cites page numbers in the two references where the analytical procedures can be found.

X ACCURACY AND PRECISION

A Of the Method

One of the criteria for choosing methods to be used for water quality analysis is that the method should measure the desired property or constituent with precision, accuracy, and specificity sufficient to meet data needs. Standard references, then, include a statement of the precision and accuracy for the method which is obtained when (usually) several analysts in different laboratories used the particular method.

B Of the Analyst

Each analyst should check his own precision and accuracy as a test of his skill in performing a test. According to the U. S. EPA Handbook for Analytical Quality Control[4], he can do this in the following manner.

To check precision, the analyst should analyze samples with four different concentrations of the constituent of interest, seven times each. The study should cover at least two hours of normal laboratory operations to allow changes in conditions to affect the results. Then he should calculate the standard deviation of each of the sets of seven results and compare his values for the lowest and highest concentrations tested with the standard deviation value published for that method in the reference book. An individual should have better values than those averaged from the work of several analysts.

To check accuracy, he can use two of the samples used to check precision by adding a known amount (spike) of the particular constituent in quantities to double the lowest concentration used, and to bring an intermediate concentration to approximately 75% of the upper limit of application of the method. He then analyzes each of the spiked samples seven times, then calculates the average of each set of seven results. To calculate accuracy in terms of % recovery, he will also need to calculate the average of the results he got when he analyzed the unspiked samples. Then:

$$\% \text{ Recovery} = \left[\frac{\text{Avg. of Spiked}}{\text{Avg. of Unspiked} + \text{Amt. of Spike}} \right] \times 100$$

Again, the individual's % recovery should be better than the published figure derived from the results of several analysts.

C Of Daily Performance

Even after an analyst has demonstrated his personal skill in performing the analysis, a daily check on precision and accuracy should be done. About one in every ten samples should be a duplicate to check precision and about one in every ten samples should be spiked to check accuracy.

It is also beneficial to participate in interlaboratory quality control programs. The U.S. EPA provides reference samples at no charge to laboratories. These samples

serve as independent checks on reagents, instruments or techniques; for training analysts or for comparative analyses within the laboratory. There is no certification or other formal evaluative function resulting from their use.

XI SELECTION OF ANALYTICAL PROCEDURES

Standard sources[1, 2, 3] will, for most parameters, contain more than one analytical procedure. Selection of the procedure to be used in a specific instance involves consideration of the use to be made of the data. In some cases, one must use specified procedures. In others, one may be able to choose among several methods.

A NPDES Permits and State Certifications

A specified analytical procedure must be used when a waste constituent is measured:

1 For an application for a National Pollutant Discharge Elimination System (NPDES) permit under Section 402 of the Federal Water Pollution Control Act (FWPCA), as amended.

2 For reports required to be submitted by dischargers under NPDES.

3 For certifications issued by States pursuant to Section 401 of the FWPCA, as amended.

Analytical procedures to be used in these situations must conform to those specified in Title 40, Chapter 1, Part 136, of the Code of Federal Regulations (CFR). The listings in the CFR usually cite two different procedures for a particular measurement.

The CFR also provides a system of applying to EPA for permission to use methods not cited in the CFR. Approval of alternative methods for nationwide use will be published in the Federal Register.

B Ambient Water Quality Monitoring

For Ambient Water Quality Monitoring, analytical procedures have not been specified by regulations. However, the selection of procedures to be used should receive attention. Use of those listed in the CFR is strongly recommended. If any of the data obtained is going to be used in connection with NPDES permits, or may be used as evidence in a legal proceeding, use of procedures listed in the CFR is again strongly recommended.

C Drinking Water Monitoring

In December, 1975, National Interim Primary Drinking Water Regulations to be effective June 24, 1977 were published in the Federal Register in Title 40, Chapter 1, Subchapter D, Part 141. The publication includes specification of analytical procedures to be used when determining compliance with the maximum contaminant levels of required parameters.

Because of the low concentrations involved in the regulations, there is often just one analytical method cited for each parameter.

Individuals or organizations may apply to EPA for permission to use methods not cited in the above. Approval of alternative methods for nationwide use will be published in the Federal Register.

XII FIELD KITS

Field kits have been devised to perform analyses outside of the laboratory. The kit may contain equipment and reagents for only one test or for a variety of measurements. It may be purchased or put together by an agency to serve its particular needs.

Since such kits are devised for performing tests with minimum time and maximum simplicity, the types of labware and reagents employed usually differ significantly from the equipment and supplies used to perform the same measurement in a laboratory.

A Shortcomings

Field conditions do not accommodate the equipment and services required for pre-treatments like distillation and digestion. Nor is it practical to carry and use calibrated glassware like burets and volumetric pipets. Other problems are preparation, transport and storage of high quality reagents, of extra supplies required to test for and remove sample interferences before making the measurement, and of instruments which are very sensitive in detecting particular constituents. One just cannot carry and set up laboratory facilities in the field which are equivalent to stationary analytical facilities.

B Uses

Even though the results of field tests are usually not as accurate and precise as those performed in the laboratory, such tests do have a place in water quality programs.

In situations where only an estimate of the concentrations of various constituents is required, field tests serve well. They are invaluable sources of information for planning a full-scale sampling/testing program when decisions must be made regarding location of sampling sites, schedule of sample collection, dilution of samples required for analysis, and treatment of samples required to remove interferences to analyses.

C NPDES Permits and State Certification

Kit methods are not approved for obtaining data required for NPDES permits or State construction certifications. If one judges that such a method is justifiable for these purposes, he must apply to EPA for permission to use it.

D Drinking Water Monitoring

The DPD test kit for residual chlorine is approved in the December, 1975 Federal Register for monitoring drinking water.

REFERENCES

1 Standard Methods for the Examination of Water and Wastewater, 14th Edition. 1976, APHA-AWWA-WPCF, 1015 18th Street, N.W., Washington, D.C. 20036

2 1975 Annual Book of ASTM Standards, Part 31, Water. ASTM, 1916 Race Street Philadelphia, PA 19103.

3 Methods for Chemical Analysis of Water and Wastes. 1974, U. S. EPA, EMSL, Cincinnati, OH 45268.

4 Analytical Quality Control in Water and Wastewater Laboratories. 1972. U. S. EPA, EMSL, Cincinnati, Ohio 45268.

This outline was prepared by A. D. Kroner, Chemist, National Training and Operational Technology Center, MOTD, OWPO, USEPA Cincinnati, Ohio 45268.

Descriptors: Analysis, Chemical Analysis, Methodology, Wastewater, Water Analysis

SAMPLE HANDLING - FIELD THROUGH LABORATORY

I PLANNING A SAMPLING PROGRAM

A Factors to Consider:

1 Locating sampling sites

2 Sampling equipment

3 Type of sample required

a grab
b composite

4 Amount of sample required

5 Frequency of collection

6 Preservation measures, if any

B Decisive Criteria

1 Nature of the sample source

2 Stability of constituent(s) to be measured

3 Ultimate use of data

II REPRESENTATIVE SAMPLES

If a sample is to provide meaningful and valid data about the parent population, it must be representative of the conditions existing in that parent source at the sampling location.

A The container should be rinsed two or three times with the water to be collected.

B Compositing Samples

1 For some sources, a composite of samples is made which will represent the average situation for stable constituents.

2 The nature of the constituent to be determined may require a series of separate samples.

C The equipment used to collect the sample is an important factor to consider. ASTM[1] has a detailed section on various sampling devices and techniques.

D Great care must be exercised when collecting samples in sludge or mud areas and near benthic deposits. No definite procedure can be given, but careful effort should be made to obtain a representative sample.

III SAMPLE IDENTIFICATION

A Each sample must be unmistakably identified, preferably with a tag or label. The required information should be planned in advance.

B An information form preprinted on the tags or labels provides uniformity of sample records, assists the sampler, and helps ensure that vital information will not be omitted.

C Useful Identification Information includes:

1 sample identity code
2 signature of sampler
3 signature of witness
4 description of sampling location detailed enough to accommodate reproducible sampling. (It may be more convenient to record the details in the field record book).
5 sampling equipment used
6 date of collection
7 time of collection
8 type of sample (grab or composite)
9 water temperature
10 sampling conditions such as weather, water level, flow rate of source, etc.
11 any preservative additions or techniques
12 record of any determinations done in the field
13 type of analyses to be done in laboratory

IV SAMPLE CONTAINERS

A Available Materials

1 glass
2 plastic
3 hard rubber

B Considerations

1 Nature of the sample - Organics attack polyethylene.

2 Nature of constituent(s) to be determined
Cations can adsorb readily on some plastics and on certain glassware. Metal or aluminum foil cap liners can interfere with metal analyses.

3 Preservatives to be used - Mineral acids attack some plastics.

4 Mailing Requirements - Containers should be large enough to allow extra volume for effects of temperature changes during transit. All caps should be securely in place. Glass containers must be protected against breakage. Styrofoam linings are useful for protecting glassware.

C Preliminary Check

Any question of possible interferences related to the sample container should be resolved before the study begins. A preliminary check should be made using corresponding sample materials, containers, preservatives and analysis.

D Cleaning

If new containers are to be used, preliminary cleaning is usually not necessary.

If the sample containers have been used previously, they should be carefully cleaned before use.

There are several cleaning methods available. Choosing the best method involves careful consideration of the nature of the sample and of the constituent(s) to be determined.

1 Phosphate detergents should not be used to clean containers for phosphorus samples.

2 Traces of dichromate cleaning solution will interfere with metal analyses.

E Storage

Sample containers should be stored and transported in a manner to assure their readiness for use.

V SAMPLE PRESERVATION

Every effort should be made to achieve the shortest possible interval between sample collection and analyses. If there must be a delay and it is long enough to produce significant changes in the sample, preservation measures are required.

At best, however, preservation efforts can only retard changes that inevitably continue after the sample is removed from the parent population.

A Functions

Methods of preservation are relatively limited. The primary functions of those employed are:

1 to retard biological action
2 to retard precipitation or the hydrolysis of chemical compounds and complexes
3 to reduce volatility of constituents

B General Methods

1 pH control - This affects precipitation of metals, salt formation and can inhibit bacterial action.

2 Chemical Addition - The choice of chemical depends on the change to be controlled.

Mercuric chloride is commonly used as a bacterial inhibitor. Disposal of the mercury-containing samples is a problem and efforts to find a substitute for this toxicant are underway.

To dispose of solutions of inorganic mercury salts, a recommended procedure is to capture and retain the mercury salts as the sulfide at a high pH. Several firms have tentatively agreed to accept the mercury sulfide for re-processing after preliminary conditions are met.(4)

3 Refrigeration and Freezing - This is the best preservation technique available, but it is not applicable to all types of samples. It is not always a practical technique for field operations.

C Specific Methods

The EPA Methods Manual(2) includes a table summarizing the holding times and preservation techniques for several analytical procedures. This information also can be found in the standard references (1, 2, 3) as part of the presentation of the individual procedures.

VI METHODS OF ANALYSIS

Standard reference books of analytical procedures to determine the physical and chemical characteristics of various types of water samples are available.

A EPA Methods Manual

The Methods Development and Quality Assurance Research Laboratory of the Environmental Protection Agency, has published a manual of analytical procedures to provide methodology for monitoring the quality of our Nation's Waters and to determine the impact of waste discharges. The title of this manual is "Methods for Chemical Analysis of Water and Wastes."(2)

For some procedures, the analyst is referred to Standard Methods and/or to ASTM Standards.

B Standard Methods

The American Public Health Association, the American Water Works Association and the Water Pollution Control Federation prepare and publish a volume describing methods of water analysis. These include physical and chemical procedures. The title of this book is "Standard Methods for the Examination of Water and Wastewater."(3)

C ASTM Standards

The American Society for Testing and Materials publishes an annual "book" of specifications and methods for testing materials. The "book" currently consists of 47 parts. The part applicable to water is a book titled, "Annual Book of ASTM Standards", Part 31, Water.(1)

D Other References

Current literature and other books of analytical procedures with related information are available to the analyst.

E Federal Register Methodology

When gathering data for National Pollutant Discharge Elimination System or State Certification report purposes, or for compliance with maximum contaminant levels in drinking water, the analyst must consult the Federal Register for a listing of approved analytical methodology. There he will be directed to pages in the above cited reference books where acceptable procedures can be found. The Federal Register also provides information concerning the protocol for obtaining approval to use analytical procedures other than those listed.

VII ORDER OF ANALYSES

The ideal situation is to perform all analyses shortly after sample collection. In the practical order, this is rarely possible. The allowable holding time for preserved samples is the basis for scheduling analyses.

A The allowable hoding time for samples depends on the nature of the sample, the stability of the constituent(s) to be determined and the conditions of storage.

1 For some constituents and physical values, immediate determination is required, e.g. dissolved oxygen, pH.

2 Using preservation techniques, the holding times for other determinations range from 6 hours (BOD) to 7 days (COD). Metals may be held up to 6 months.[2]

3 The EPA Methods Manual[2] and Standard Methods[3] include a table summarizing holding times and preservation techniques for several analytical procedures. This information can also be found in the standard references [1, 2, 3] as part of the presentation of the individual procedures.

4 If dissolved concentrations are sought, filtration should be done in the field if at all possible. Otherwise, the sample is filtered as soon as it is received in the laboratory. A 0.45 micron membrane filter is recommended for reproducible filtration.

B The time interval between collection and analysis is important and should be recorded in the laboratory record book.

VIII RECORD KEEPING

The importance of maintaining a bound, legible record of pertinent information on samples cannot be over-emphasized.

A Field Operations

A bound notebook should be used. Information that should be recorded includes:

1 Sample identification records (See Part III)

2 Any information requested by the analyst as significant

3 Details of sample preservation

4 A complete record of data on any determinations done in the field. (See B, next)

5 Shipping details and records

B Laboratory Operations

Samples should be logged in as soon as received and the analyzes performed as soon as possible.

A bound notebook should be used. Preprinted data forms provide uniformity of records and help ensure that required information will be recorded. Such sheets should be permanently bound.

Items in the laboratory notebook would include:

1 sample identifying code
2 date and time of collection
3 date and time of analysis
4 the analytical method used
5 any deviations from the analytical method used and why this was done
6 data obtained during analysis
7 results of quality control checks on the analysis
8 any information useful to those who interpret and use the data
9 signature of the analyst

IX SUMMARY

Valid data can be obtained only from a representative sample, unmistakably identified, carefully collected and stored. A skilled analyst, using approved methods of analyses and performing the determinations within the prescribed time limits, can produce data for the sample. This data will be of value only if a written record exists to verify sample history from the field through the laboratory.

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This outline was prepared by Audrey D. Kroner, Chemist, National Training and Operational Technology Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268

Descriptors: On-Site Data Collections, On-Site Investigations, Planning, Handling, Sample, Sampling, Water Sampling, Surface Waters, Preservation, Wastewater

ATOMIC ABSORPTION SPECTROPHOTOMETRY

I INTRODUCTION

Atomic absorption spectroscopy has been well known to physicists and astronomers for more than 100 years. In 1850, Kirchoff took light from the sun and collimated it with a lens through the flame of an ordinary laboratory burner, and then passed the light through a prism which dispersed it into the characteristic visible spectrum with which we are all familiar. He then took a platinum spoon containing a sodium salt and introduced it into the flame. He observed that the yellow light that was present in the spectrum disappeared and in its place appeared the characteristic resonance lines of sodium. Since then astronomers have used the technique to detect and measure the concentration of metals in the vapors of stars. In 1953, Walsh[1] recognized its potential advantage over emission spectroscopy for trace metal analysis. He designed and built an analytically useful atomic absorption instrument. Shortly thereafter the advantages of atomic absorption instrumentation were recognized in the United States.

II THEORY

The basis of the method is the measurement of the light absorbed at the wavelength of a resonance line by the unexcited atoms of the element. Elements not themselves excited to emission by a flame may be determined in a flame by absorption provided that the atomic state is capable of existence.

At the temperature of a normal air-acetylene flame (2100°C) only about one per cent of all atoms is excited to emission in a flame; therefore absorption due to a transition from the ground electronic state to a higher energy level is virtually an absolute measure of the number of atoms in the flame, and the concentration of the element in the sample. Electrons will absorb energy at the same characteristic wavelength at which they emit energy. This is the principle upon which the technique of atomic absorption spectroscopy is based.

The advantages of atomic absorption spectroscopy as compared to emission spectroscopy are: (1) that atomic absorption is independent of the excitation potential of the transition involved and (2) that it is less subject to temperature variation and interference from extraneous radiation and interference from extraneous radiation or energy exchange between atoms.

Atomic absorption analytical apparatus (Figure 1) consists of a suitable source of light emitting the line spectrum of an element, a device for vaporizing the sample, a means of line isolation (monochomator or filter) and photoelectric detecting and measuring equipment.

If the detector is placed to receive only the resonance line of the element from the light source, measurement can be made of the absorption of resonance-line radiation on its passage through the vaporized sample. The magnitude of this absorption gives a measure of the concentration of free ground-state atoms of the element in the vapor and when referred to a calibration curve, provides a means of determining the concentration of the element in the sample.

III INSTRUMENTATION

The general arrangement of an absorption flame photometer is no different from an emission flame photometer except for the addition of a light source. An aerosol is introduced into a flame which is placed on the optical axis between the entrance slit of the monochromator and the monochromatic light source. Energy of the wavelength absorbed by the sample is provided by a source lamp whose emitting cathode is made of that element. This energy is passed through the flame and then through a dispersing device. A detector measures the absorbed and unabsorbed exciting radiation.

A Light Source

For the more volatile elements such as the alkali metals, mercury and thallium,

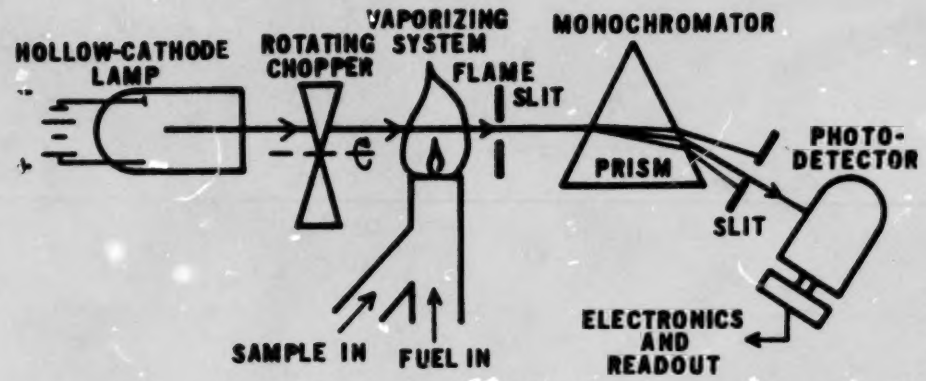

FIGURE I

the most convenient source is the spectral vapor lamp, which consists of a closed glass or silica tube, into which are sealed oxide-coated electrodes, containing one of the rare gases and some of the appropriate metals. For line sources of the less-volatile elements, hollow-cathode discharge tubes have been found the most satisfactory. These consist of an anode and hallow cylindrical cathode (either composed of or lined with the appropriate metal) mounted in a sealed glass tube containing one of the rare gases (helium or argon).

Lamps are operated at low currents to improve linearity of response and maintain narrow emission lines.

B Vaporization of Sample

1 Atomic-absorption methods have been applied almost exclusively to the analysis of solutions and for this purpose flames, fed with a fine spray of the sample solution, similar to those employed in flame photometry are used.

The burner has two principal functions to perform:

a It must introduce the sample into the flame.

b It must reduce the metal to the atomic state.

2 Burners can be classified as:

a Total-consumption

Those which introduce the sample spray directly into the flame. (Figure 2)

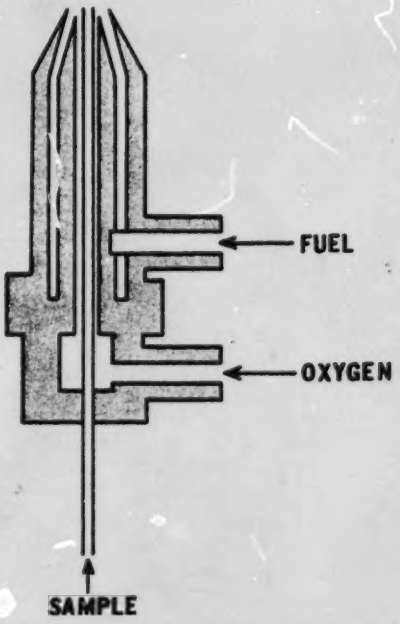

FIGURE 2

4-2

b Premix

Those which introduce the spray into a condensing chamber for removing large droplets. (Figure 3)

3 Flame shape is important. The flame should have a long path length (but a narrow width, such as a fishtail flame) so that the source traverses an increased number of atoms capable of contributing to the absorption signal.

4 The effective length of the flame may be increased by multiple passages through the flame with a reflecting mirror system, or by alignment of several burners in series.

5 The flame temperature need only be high enough to dissociate molecular compounds into the free metal atoms.

Typical flame temperatures are shown in Table I.

Table I

Fuel-Oxidant	Approximate Temp., °C
Nitrous Oxide - acetylene	3000
Hydrogen - air	2100
Hydrogen - oxygen	2700 - 2800
Acetylene - oxygen	3100
Acetylene - air	2000 - 2200
Propane - oxygen	2700 - 2800
Illuminating gas - oxygen	2800
Cyanogen - oxygen	4900

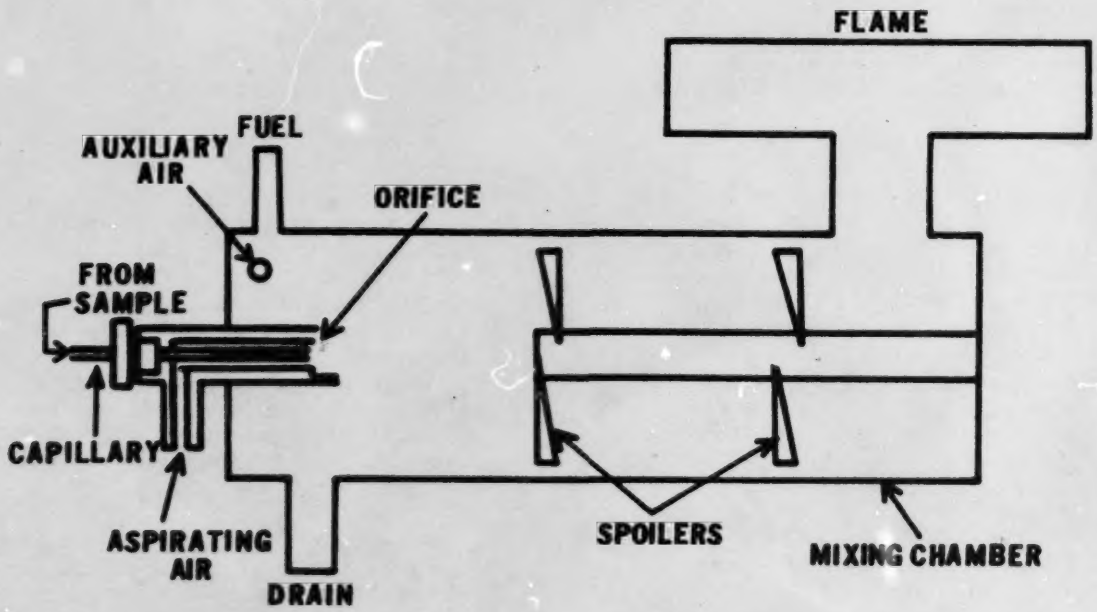

Figure 3

4-3

C Line Isolation

1 The use of a line spectrum of the element being determined, rather than a continuous spectrum, makes possible the use of monochromators of low resolving power or even filters. When a spectral lamp is used as a light source, it is only necessary to isolate the resonance line from neighboring lines of the light source or vaporized sample. The resolution of the method is implicit in the width of the emission and absorption lines.

2 To realize the full potentialities of the method, the strongest absorption line must be used. For elements with simple spectra, the resonance line arising from the lowest excited state is usually the line exhibiting strongest absorption.

3 Calibration curves depart from linearity at much lower concentrations in absorption work as compared with emission work. Curvature results partly from increased pressure broadening as the concentration of salt rises, but also depends on source characteristics, particularly self-absorption, and on the nature and homogeneity of the flame.

D Detection

1 Photo-electric detectors used in atomic absorption analysis need be no more sensitive than those used in emission analysis, since in the atomic absorption method, concentration of an element is determined by measuring the reduction in intensity of the resonance line emitted from a source of high intensity.

2 Single or double-beam circuits may be adopted for work with a single beam instrument, results are directly dependent upon source and detector stability. Both must be powered by separate power supplies. In a double-beam system small variations in the source signal are compensated automatically.

IV EVALUATION

A Sensitivity

1 For an air-acetylene flame of length 2 or 3 cm the lower limits of detection of elements having low resonance-line excitation potential (eg Na-K) are approximately equal in a single-beam atomic absorption and emission methods.

2 For elements having highly reversed resonance lines or resonance lines of high excitation potential, the atomic-absorption method has decided advantages over emission methods. Examples of elements in these categories are Zn, Mg, Fe and Mn.

3 A disadvantage of the atomic-absorption method, when compared with flame emission, is the lack of a quick and simple method of varying sensitivity to deal with solutions of widely varying element concentrations. The sensitivity of an atomic-absorption instrument is determined almost entirely by flame characteristics, notably length of light path through the flame.

4 A comparison of sensitivity obtained by emission and adsorption techniques is given in Table II.

B Precision

1 Precision of a single-beam atomic absorption instrument is primarily a function of the stability of light output from the spectral lamp. This in turn is dependent on the stability of the main supply and inherent stability of the lamp. The largest fluctuations are only $\pm$ 2 percent for the hollow cathode tube and sodium spectral vapor lamp. A double-beam instrument significantly reduces this error.

2 In common with flame-emission methods, atomic absorption is subject to "noise" from the flame and the detector. Changes in absorption caused by fluctuations in

Element	Sensitivity mg/l Flame	A.A
Aluminum	2	0.5
Antimony		0.2
Arsenic		1.0
Barium	0.3	1.0
Beryllium	25	0.05
Bismuth		0.2
Cadmium	2	0.01
Calcium	0.003	0.01
Cesium		0.05
Chromium	0.1	0.01
Cobalt		0.15
Copper	0.01	0.005
Gallium		1.0
Gold		0.1
Imdium		0.5
Iron	0.2	0.05
Lead	2	0.15
Lithium	0.002	0.005
Magnesium	0.1	0.003
Manganese	0.01	0.01
Mercury	10	0.5
Molybdenum		0.2
Nickel		0.05
Palladium		1.0
Platinum		0.5
Potassium	0.001	0.005
Rhodium		0.3
Rubidium		0.02
Selenium		1.0
Silver	0.05	0.02
Sodium	0.002	0.005
Strontium	0.01	0.02
Tellurium		0.5
Titanium		1.0
Thallium		0.2
Tin		2.0
Vanadium		0.5
Zinc	200	0.005

Table II

flame temperature are much less than those in emission because the strength of the absorption line is principally dependent on Doppler width whereas the intensity of emission from the flame is much more sensitive to temperature.

C Accuracy

This is shown by the types of interference found in flame emission and atomic absorption spectroscopy. There are three types:

1 Physical

Collision of atoms and electrons or atoms and molecules will transfer energy thus causing an enhancement or depression of analysis-line emission.

This has a large effect on flame emission analysis but has only a negligible effect on atomic absorption.

2 Radiative

Light from elements other than the one being measured pass the line isolating device (monochromator or filter). This occurs in flame emission work, for example, the interference of calcium and magnesium in sodium determinations. This interference is also encountered in atomic absorption using a D.C. system but is very small because of the large signal from the hollow-cathode tube. Radiative interference is eliminated in an A.C. system.

3 Chemical

Emission from an element in the flame is depressed by the formation of compounds, which are not dissociated at flame temperatures. This also affects absorption because the formation of temperature - stable compounds in the flame causes proportionate reduction in the population of ground-state and excited atoms.

Investigations to date suggest chemical interference is confined, almost entirely, to the alkaline-earth elements and that calcium absorption is more subject to this interference than is magnesium absorption.

Typical calibration curves are shown in Figure 5.

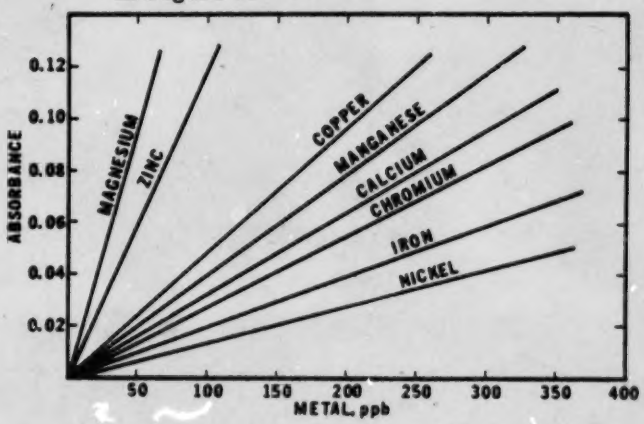

Figure 5

V REMOVAL OF INTERFERENCES AND CONCENTRATION OF SAMPLE

A Removal of Interferences

1 The methods for overcoming these interferences in atomic absorption are similar to those used in flame emission, namely, either separation of interfering ions or suppression of the interference by addition in excess of a substance that will prevent formation of compounds between interfering ions and the element being determined.

B Concentration of Sample

1 Organic separations can be used to concentrate a sample. Interferences are removed, as seen above, and also the organic solvent enhances the absorption.

2 Ion exchange has also been used successfully for concentrating samples for atomic absorption.

VI CONCLUSIONS

Atomic absorption methods are as good as or better than emission methods, for elements to which they can both be applied, in sensitivity, precision and accuracy. They can be applied to a far wider range of elements than can emission analysis. The additional cost of hollow cathode discharge tubes is compensated by the greater range of analyses and greater reliability of results.

VII INSTRUMENTS AVAILABLE

A Perkin Elmer

1 Model 303 - double beam, AC - $5,920.00

1 Model 290 - single beam, AC - $2,900.00

B Beckman attachments for existing spectrophotometers

1 Use with model D.U. and D.U.-2- single beam, DC - $2,135.00

2 Use with model D.B. - single beam, AC - $2,495.00

C Jarrell-Ash

1 Dual atomic absorption flame spectrometer- single beam, AC - $5,800.00

D E.E.L.

1 Atomic absorption spectrophotometer - single beam, AC - $2,850.00

ACKNOWLEDGEMENT

Certain portions of this outline contain training meterial from a prior outline by Nathan C. Malof.

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This outline was prepared by P. F. Hallbach, Chemist, National Training Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Analytical Techniques, Atomic Absorption, Instrumental Analysis, Metals Analysis

ENERGY SOURCES FOR ATOMIC ABSORPTION SPECTROSCOPY

I INTRODUCTION

The basic principle behind atomic absorption spectroscopy can be said to be opposite that of emission methods. In emission spectroscopy the sample is raised to a meta stable excited energy level by an input of energy. Then the sample is allowed to return to its stable ground state. When the sample returns to its ground state energy is given off and a high proportion of this energy is at a wavelength characteristic of the metal in the sample that is being analyzed.

In atomic absorption the element under investigation is not excited but is merely dissociated from its chemical bonds, and in an unexcited ground state. It is then capable of absorbing radiation at a characteristic wavelength, i.e., the same wavelength as would be emitted if the element were excited.

This difference affects both the sensitivity and stability of results obtained in analyzing for elements via atomic absorption. Due to the fact that, even at optimum conditions in emission spectroscopy, for every atom available in an excited state there are many more available in the unexcited state. For example, for every calcium atom in the excited state there are about a thousand dissociated and accessible to atomic absorption. For zinc the ratio is even greater, for every one atom that is excited there are 10^9 available for atomic absorption.

These numbers do not indicate a direct proportional increase in sensitivity. Some increase is noticed but not as large as the numbers indicate. In addition to the sensitivity increase, an increase in the stability is also obtained. If during analysis of zinc by emission spectroscopy a change in flame would make available another atom, a change of 100% in the emission value has occurred but the change in atomic absorption would not be significant.

In order to provide energy that the unexcited atoms are capable of absorbing, a hollow cathode lamp is used in atomic absorption. Hollow cathode lamps are manufactured by several firms and the shape of the lamp has little to do with its function. Basically, a hollow cathode lamp is composed of an anode, cathode, shielding, envelope, end window and a filler gas.

To provide energy at the specific wavelength needed for the element under analysis the hollow cathode lamp has its cathode constructed from or lined with the element of interest usually in the shape of a cylinder closed at one end. As each lamp emits the line spectra of the element present in its cathode, a different lamp is usually used for each element analyzed.

Each hollow cathode lamp operates under the same general principle. The lamp envelope is filled with an inert gas, usually argon or neon, at a low pressure (1 to 10 mm Hg). Once sufficient voltage is applied across the electrodes within the lamp, the inert gas ionizes and current begins to flow. When this happens positive gas ions bombard the cathode and heating occurs. As the inner surface of the cathode heats, it sputters and metal vapor fills the cathode volume. Charged gas particles collide with the metal atom, raising its valence electrons to higher energy states. When these excited electrons return to their ground state, they emit light. The spectrum thus emitted contains the same wavelengths of light required for absorption by that metal atom under analysis. As many cathodes are alloyed to obtain mechanical strength and as the gas fill is also excited, the emission of a hollow cathode lamp contains the spectra of more than one element.

Another step to increase the usefullness of a hollow cathode lamp was to incorporate more than one element into the cathode so the lamp could be used for more than one element. This has been done and there are available lamps that contain as many as six elements. Not all elements can be usefully combined in multi-element lamps.

Some combinations are difficult or impossible from a metallurgical viewpoint. More important to the user, some combinations, though feasible to manufacture, yield spectral interferences. Here the emission lines from one element lie

too close to those of another element, so that spurious absorption signals can results, if the second element is also present in the sample.

When three or more elements are combined in a lamp, it is also frequently true that the emission from the individual elements is not as bright as that from single-element lamps. However, one chief advantage lies in the cost. A multi-element lamp is not proportionately as expensive as a single-element lamp. Also, the curves of absorbance versus concentration obtained with multi-element lamps may be less linear than those from single element sources, particularly at high absorptions.

The operating current of a hollow cathode lamp can be a critical parameter in optimizing an atomic absorption measurement. Lamp intensities and resulting absorbance in the flame do not change linearly with operating current. Typically high absorbance and good signal-to-noise ratios are obtained at current near one-third the maximum lamp currents. Increasing the hollow cathode lamp current will increase its output intensity. But sensitivity is reduced through line broadening and/or self reversal for some elements. As a result, we can expect better sensitivity at lower lamp currents.

Most manufacturers will provide a rated maximum current beyond which the lamp should not be operated. Any operation above this current produces the danger of destruction of the cathode. It is best to follow the manufacturer's suggested operational current when using its lamp. If warm-up of the lamp is necessary, as in a single beam spectrophotometer this can be done at currents below the operating current, bringing the lamp to proper current just before use. Lamp current will affect lamp life. Experimental data have shown that lamp life is reduced by the square of the current increase. Thus, lower lamp current can only improve the performance and life of a hollow cathode lamp.

Each hollow cathode lamp will have a different warm-up time which can vary from 5 to 20 minutes. Use of a lamp in a single beam instrument will require a warm-up time but a double beam instrument does not require this waiting period. The use in some instruments of multiple-lamp turret assembly facilitates the operation of many lamps at different operating currents to speed the time of analysis by eliminating warm-up time when lamps are changed. In single beam instruments a multi-element lamp is attractive because all its elements are ready when one element is ready.

Lamp life is hard to estimate; however, most manufacturers guarantee their lamps for a use period of five ampere hours. When this figure is divided by typical operating currents, the average guarantee extends to between 300 and 500 hours of use. In practice, most lamps last a great deal longer. If lamps are not used regularly, it is wise to operate them for at least one hour per month on normal current in order to reduce the possibility of fluctuation when the lamp is finally put into use.

II SUMMARY

In atomic absorption spectroscopy, the hollow cathode lamp is perhaps the most important component. The usefulness of a given analysis depends directly on the brightness, spectral purity and stability of the lamp. Also, the economic feasibility of owning atomic absorption equipment is often closely tied to hollow cathode lamp life.

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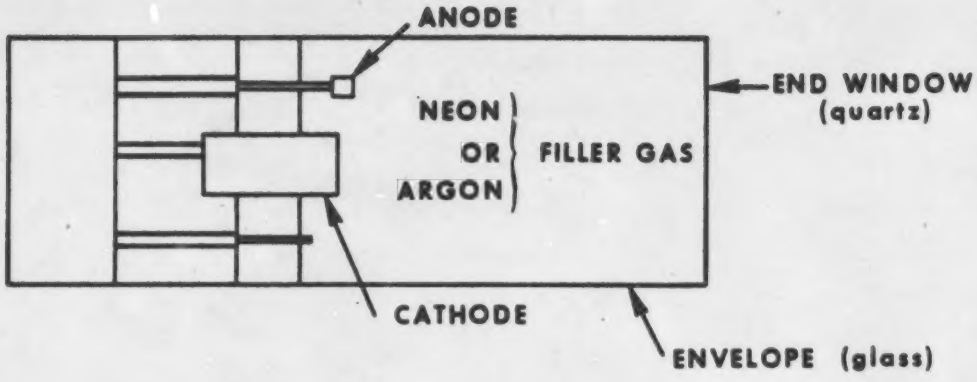

HOLLOW CATHODE LAMP
FIGURE 1

This outline was prepared by J. D. Pfaff, National Training Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Spectroscopy, Spectrophotometers

BURNERS AND FUEL MIXTURES

I INTRODUCTION

The object of the burner and its fuel and oxidant gases on an atomic absorption spectrophotometer is to produce in the flame a supply of dissociated atoms in their ground or unexcited state. These atoms will then be available to absorb the energy provided by the hollow cathode lamp.

II BURNERS

There are generally two classifications of burners for atomic absorption. These are the total consumption burner and the pre-mix or laminar flow burner. These burners have been covered in the outline on the Fundamentals of Atomic Absorption. This outline includes diagrammatic drawings of the two types.

The total consumption burner is primarily used in flame photometry and when atomic absorption came into existence the first attempt was to use this type burner. However, it has some severe limitations when applied to atomic absorption. Consequently, experimentation with various forms of burners led to what is now the pre-mix or laminar burner.

Most manufacturers today use the pre-mix type burner with some different modifications as the standard burner on their atomic absorption instruments. These burners are a three part system. They contain an independent nebulizer for sample introduction, a pre-mix chamber and a burner head.

Any burner design whether different by principle or manufacturer's design should have certain criteria. The burner should be stable, its absorption for a given concentration should remain constant for as long as is possible. A burner should also be quiet, both audibly and instrumentally and not cause fluttering or wavering in the output. Burners should have as little carry over from one sample to the next. They should also be easy to clean and not easily corroded.

Usually the pre-mix type of burner will have the better results when the above criteria is compared between it and the total consumption burner. All these parameters can also vary from manufacturer to manufacturer and thought should be given when a new instrument is contemplated or accessory equipment for existing instrumentation purchased.

A Nebulizer

The nebulizer is simply a device used to asperate the sample into the burner and from there into the flame. This device works on a venturi effect with the oxidant being moved across the tip of a stainless steel capillary tube. This causes a pressure drop along the capillary's length. When the other end of the tube is immersed in a liquid, that liquid will be drawn through the tube and discharged in the oxidant stream where it is blown into a fine aerosol.

The rate of asperation is controlled by adjusting the position of the end of the capillary with respect to the oxidant flow. A typical optimum flow rate is approximately 5 milliliters per minute. Most manufacturers provide some kind of adjustment device usually located on the front of the burner which is used to adjust the flow rate.

B Pre-Mix Chamber

When the sample leaves the nebulizer section, it is mixed with more oxidant and fuel and mixed again in the body of the burner itself. All droplets of sample too heavy to progress into the burner head are collected by the baffling and sides of the burner and flow down the drain into the waste collection vessel. This wasted portion of the sample can typically amount to ninety percent of that asperated into the burner. The pre-mix section should be made of some material which will resist corrosion.

The drain outlet of the burner should be connected to some type of drain receptacle

lower than the instrument itself. The manufacturer's directions for connecting this drain should be followed closely—most instruments provide a positive water seal somewhere in the system. This is done to prevent flashbacks in the burner. Care should also be taken to follow the manufacturer's directions for cleaning both the nebulizer, mixing chamber, and burner head.

C Burner Head

The third part of the burner is the burner head. Most instruments are so designed to allow a quick change of the head, of course caution should be taken that the head being removed has had sufficient time to cool. In most cases the burner head and burner body have some locking device which will not allow certain type heads to be used with various gas mixes. For example, the Boling head should not be used with nitrous oxide-acetylene gases and the collar or locking device helps to prevent this from accidentally being done.

There are basically three types of burner heads with many variations of these three for specific needs. This is partially due to the manufacturers finding new ways to improve the design of the heads. The three types of heads are the Boling head, the nitrous oxide head and a type of burner head designed to allow the analysis of samples with high solids content.

1 Boling burner head (Figure 1)

The Boling burner is distinctive in appearance, having three separate longitudinal orifices or slits at the top of a compressed chamber with a triangular cross section. This design provides a long, flat flame which is actually composed of three flames which are separately supported and distinct at the base. This burner can be used with air-acetylene, air-hydrogen, air-propane or argon-hydrogen flames. It can burn concentrated solutions without clogging and provides better sensitivities for many metals. Many manufacturers provide this burner head as the standard head for their instruments.

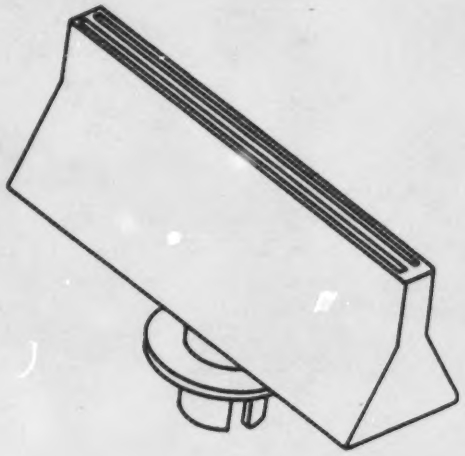

Figure 1
Boling Burner Head

2 Nitrous oxide head

The nitrous oxide burner head is, as its name implies, used for elements which need the hotter flame to atomize and for the metals which readily form oxides in the flame and for the rare earth elements. The elements included in the USEPA manual of Methods for Chemical Analysis of Water and Wastes that are to be determined by atomic absorption are listed in Table I. There are six elements that must be determined by the use of the nitrous oxide-acetylene flame in order to attain sufficient sensitivities to meet the NPDES standards.

Figures 2 and 3 show two types of nitrous oxide heads. They are both characterized by a thick head and a short slot (5 cm). Instrumentation Laboratory adds fins on both sides of the head to aid in cooling and two trenches along the slot to increase ambient air flow and reduce carbon buildup.

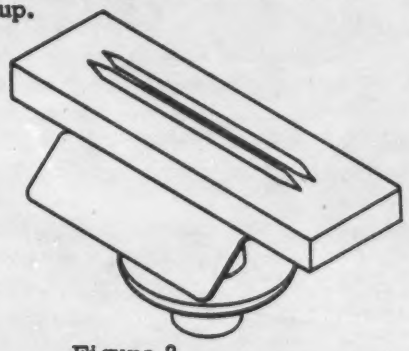

Figure 2
Instrumentation Laboratory
Nitrous Oxide Burner Head

Figure 3
Perkin-Elmer
Nitrous Oxide Burner Head

3 High solids head

This head looks similar to the nitrous oxide head with the main difference being the slot. The slot on the high solids burner is both longer and wider. The prime purpose of this burner head is to allow analysis of one element in the presence of overwhelming amounts of another element. The head should be used with the air-acetylene flame and not with the nitrous oxide as danger of flash-back would exist. Other heads are made for more specific purposes by each manufacturer and reference should be made to the particular literature of the manufacturer of the burner head.

III GASES (FUEL AND OXIDANT)

Table I shows that for the metals listed in the Federal Register as being capable of analysis by atomic absorption, only two fuel oxidant mixtures are listed. Nitrous oxide and acetylene-air can be used to analyze most of the metals. The air-acetylene combination is not hot enough to dissociate most of the compounds of a number of elements such as aluminum, boron and silicon, and it incompletely dissociates those of other metals like chromium, molybdenum and barium. An additional problem is that the refractory elements are quick to form stable oxides.

Some exceptions are noted to the fuel mixtures noted above. These metals are easily dissociated and other means can be used. For example, the analysis of mercury is accomplished without a flame and arsenic and solenium are done using an argon-hydron flame in the gaseous hydride procedure.

When using the nitrous oxide-acetylene flame a note on the safety of operation should be added. Although not difficult to use, with modern atomic absorption instruments this gas combination is somewhat more likely to flash-back than air-acetylene when not used in accordance with instructions.

Table I in the outline on the Fundamentals of Atomic Absorption gives the burning temperatures of most fuel oxidant mixtures. Some of the combinations are not used in atomic absorption but are included as a means of comparison.

IV SUMMARY

Each manufacturer of atomic absorption instrumentation equips its instruments with a standard bur[illegible]ad. Should the user desire, he can purc[illegible]litional burner heads. These are equipped with a common connector to the burner body and no great problem exists to change from one head to another. There are basically two burners, the total consumption and the laminar flow or pre-mix type.

The pre-mix type can utilize a number of heads such as the Boling, nitrous oxide or high solids each of which have specific uses.

Table I shows the metal elements of which the NPDES program permits analysis by atomic absorption and the fuel oxidant mixture recommended for its analysis. Two mixtures are of primary importance, that is the air-acetylene and nitrous oxide-acetylene mixtures.

TABLE I

Methods in USEPA Methods Manual

1	Aluminum	Nitrous Oxide	Acetylene
2	Antimony	Air	Acetylene
3	Arsenic	Gaseous Hydride Method	Acetylene
4	Barium	Nitrous Oxide	Acetylene
5	Beryllium	Nitrous Oxide	Acetylene
6	Cadmium	Air	Acetylene
7	Calcium	Air	Acetylene
8	Chromium	Nitrous Oxide	Acetylene
9	Cobalt	Air	Acetylene
10	Copper	Air	Acetylene
11	Iron	Air	Acetylene
12	Lead	Air	Acetylene
13	Magnesium	Air	Acetylene
14	Manganese	Air	Acetylene
15	Mercury	Cold Vapor Technique	Acetylene
16	Molybdenum	Nitrous Oxide	Acetylene
17	Nickel	Air	Acetylene
18	Potassium	Air	Acetylene
19	Selenium	Gaseous Hydride Method	Acetylene
20	Silver	Air	Acetylene
21	Sodium	Air	Acetylene
22	Thallium	Air	Acetylene
23	Tin	Air	Acetylene
24	Titanium	Nitrous Oxide	Acetylene
25	Vanadium	Nitrous Oxide	Acetylene
26	Zinc	Air	Acetylene

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This outline was prepared by J. D. Pfaff, National Training Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Spectroscopy, Spectrophotometers

ATOMIC ABSORPTION - THE GRAPHITE FURNACE

I INTRODUCTION

Basically atomic absorption utilizes the idea that metallic compounds in a sample are introduced into a flame where they are dissociated and then converted to their atomic ground state. These atoms then absorb light energy from a hollow cathode lamp. The amount of absorption is proportional to the concentration of the material being analyzed in the sample.

The graphite furnace replaces the burner as the generator of atoms in the procedure mentioned above. The general rule of thumb is to use the flame wherever possible for analysis. However, there are certain advantages and disadvantages with both pieces of equipment.

A Advantages

When only small amounts of sample are available and several metals are to be analyzed, the graphite furnace is the choice. Typical sample volumes used run from 5 to 100 microliters. Consequently, even a 50 ml sample could be used for a number of analyses.

In general, less preparation time is needed to obtain a furnace ready sample. In order to determine a total metal, no chemical extraction step would be necessary for certain metals as they could be run directly in the furnace.

The furnace procedure is more sensitive than the flame. This can be in an order of magnitude range (see Table I for some examples) that is from 100 to 1000 times. This means that in many cases preconcentration is not necessary to reach the level that must be detected.

Depending on what the analysis is being run for, liquid samples having finely divided solids do not have to be completely in solution. The furnace can handle samples that would clog the burner.

B Disadvantages

The first and most obvious disadvantage associated with the furnace is cost. The furnace is an option that must be purchased separately and will cost thousands of dollars more. The flame is a normal part of the instrument and adds no extra cost.

When compared to direct aspiration into the flame and not considering any pretreatment, the flame is faster. Once aspirated, the result is only several seconds away. However, due to the steps involved in obtaining a dry, chared and atomized sample with the furnace, several minutes are necessary to obtain results. So when doing aqueous samples which need no pretreatment the flame will be much faster.

Most of the interferences connected with the use of the flame in atomic absorption are well understood and can be compensated for, however, this is not true with furnace techniques. The user of the furnace must understand the operation and what is going on during the various steps and constantly be on the alert for interferences. As mentioned, the complete make-up of the sample can affect the results of the analysis. The dissolved solids, larger concentration of salts, organics, all may affect the analyses of a sample by the furnace. Consequently, the standards should be as close to the same matrix make-up as possible.

II GENERAL

The spectrophotometer portion of the system remains the same. However, the sample introduction and atomization methods are changed. The aspirator and burner are replaced by an electricly heated graphite furnace.

The sample is usually not introduced by a continuous aspiration but in discrete

TABLE 1

Atomic Absorption Concentration Ranges[1]

	Direct Aspiration			Furnace Procedure[4,5]	
Metal	Detection Limit mg/l	Sensitivity mg/l	Optimum Concentration Range mg/l	Detection Limit ug/l	Optimum Concentration Range ug/l
Aluminum	0.1	1	5 - 50	3	20 - 200
Antimony	0.2	0.5	1 - 40	3	20 - 300
Arsenic[2,3]	0.002	-	0.002 - 0.02	1	5 - 100
Barium(p)	0.1	0.4	1 - 20	2	10 - 200
Beryllium	0.005	0.025	0.05 - 2	0.2	1 - 30
Cadmium	0.005	0.025	0.05 - 2	0.1	0.5 - 10
Calcium	0.01	0.08	0.2 - 7	-	- -
Chromium	0.05	0.25	0.5 - 10	1	5 - 100
Cobalt	0.05	0.2	0.5 - 5	1	5 - 100
Copper	0.02	0.1	0.2 - 5	1	5 - 100
Gold	0.1	0.25	0.5 - 20	1	5 - 100
Iridium(p)	3	8	20 - 500	30	100 - 1500
Iron	0.03	0.12	0.3 - 5	1	5 - 100
Lead	0.1	0.5	1 - 20	1	5 - 100
Magnesium	0.001	0.007	0.02 - 0.5	-	- -
Manganese	0.01	0.05	0.1 - 3	0.2	1 - 30
Mercury[3]	0.0002	-	0.0002 - 0.01	-	- -
Molybdenum(p)	0.1	0.4	1 - 40	1	3 - 60
Nickel(p)	0.04	0.15	0.3 - 5	1	5 - 100
Osmium	0.3	1	2 - 100	20	50 - 500
Palladium(p)	0.1	0.25	0.5 - 15	5	20 - 400
Platinum(p)	0.2	2	5 - 75	20	100 - 2000
Potassium	0.01	0.04	0.1 - 2	-	-
Rhenium(p)	5	15	50 - 1000	200	500 - 5000
Rhodium(p)	0.05	0.3	1 - 30	5	20 - 400
Ruthenium	0.2	0.5	1 - 50	20	100 - 2000
Selenium[2]	0.002	-	0.002 - 0.02	2	5 - 100
Silver	0.01	0.06	0.1 - 4	0.2	1 - 25
Sodium	0.002	0.015	0.03 - 1	-	- -
Thallium	0.1	0.5	1 - 20	1	5 - 100
Tin	0.8	4	10 - 300	5	20 - 300
Titanium (p)	0.4	2	5 - 100	10	50 - 500
Vanadium (p)	0.2	0.8	2 - 100	4	10 - 200
Zinc	0.005	0.02	0.05 - 1	0.05	0.2 - 4

(1) The concentrations shown are not contrived values and should be obtainable with any satisfactory atomic absorption spectrophotometer.
(2) Gaseous hydride method.
(3) Cold vapor technique.
(4) For furnace sensitivity values consult instrument operating manual.
(5) The listed furnace values are those expected when using a 20 ul injection and normal gas flow except in the case of arsenic and selenium where gas interrupt is used. The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

amounts by a pipet. Unless an automatic sampler is attached to the instrument (optional equipment) the operator of the instrument introduces from about 5 to 100 microliters of the material to be measured. This pipeting is a technique and how it is carried out will affect the reproducibility of the procedure. The micro-pipets should be accurate and deliver a reproducible amount. They are available from several chemical supply houses and usually from instrument manufacturers.

After the sample has been added the pre-selected program is begun. An inert purge gas flow is initiated and flows through the graphite tube. This purge gas is used to protect the tube from air oxidation as well as to sweep materials out of the tube. The purge gas flows throughout the program in some instruments, unless specifically stopped by the operator.

Usually the program is in three to four steps. These are the drying, charing, atomization and perhaps a clean-up step. During each step the temperature of the graphite tube is increased. The furnace is cooled by water to protect it against overheating and to return the tube to starting temperature before the next run. In the atomization step, the atomic absorption reading is taken by passing light from a hollow cathode lamp through the graphite tube and measuring the amount of absorbed light.

Most instruments have some form of display which indicates the absorption or if calibrated, the concentration of the measured sample. Consequently, a recorder is not a necessity. However, much valuable information can be gained by having a recorder in operation during the program sequence. In addition a hard copy of the results is available to the operator. It is recommended that a recorder be available for use with the instrument.

A The Graphite Tube

The general workings of the graphite furnace have been discussed. Now let's look closer at each portion of the furnace. The graphite tube's configuration varies with each manufacturer. It is usually a cylindrical tube open at both ends and has an opening near mid-point for sample introduction. The tube is usually surrounded by some device which will facilitate cooling by the use of a flow of water and is heated by electrical contacts.

The size and consequently the amount of sample capable of being used varies considerably with manufacturers. Internally the tube may have grooves or threads in order to more easily retain the sample in the center portion of the tube specificly when organic solvents are used. Some manufacturers utilize a cup type of tube which is open on top and capable of holding larger amounts of sample than their tube. Sample size limits vary from about 5 μl to 100 μl. Organic solvents may be used in the furnace, however, usually smaller sample sizes must be used due to the solvent tending to spread more easily in the tube.

Tubes are available from most manufacturers and for some instruments that are pyrolyticly coated. The advantages of this coating is to increase tube-life, it also helps to prevent diffusion of the sample through the porous graphite and it stops formation of carbides. The pyrolytic coating helps to prevent the sample from soaking into the graphite and helps to reduce memory effects. Experience has shown that additional burns are necessary to clean-up a new pyrolytic tube than a non-pyrolytic tube. In addition, some elements seem to lose precision when analyzed in pyrolytic tubes. The user is cautioned to check this for himself or seek advice from the manufacturer of their instrument on the use of pyrolytic tubes.

The lifetime or number of burns for which a tube can be used will vary considerably. This is dependent upon the program used

in the analyses, the amount of oxygen present in the inert gas used and the type of sample being analyzed. A typical range of burns per tube would vary from 30 to 300 before it is replaced. If the program used incorporates long atomization times at high temperatures, the tube will have a short life time. The amount of oxygen as an impurity in the inert gas will quickly lower the lifetime. As a tube ages, the precision of the results from that tube may also decrease.

B Inert or Purge Gas

Argon and nitrogen are the two gases used for protection of the graphite tube and analyte from rapid oxidation due to air oxidation. The choice of which to use is determined by recommendation of the instrument manufacturer. However, several things must be kept in mind.

The purity grade of gas available to the user. Argon is usually more readily available in an oxygen and moisture-free grade than is nitrogen. A gas containing even small amounts of oxygen can decrease sensitivity and shorten the graphite tube lifetime. In addition, some elements have shown an increase in sensitivity when argon is used. When nitrogen is used at high temperatures, molecules of cyanogen may be formed in the furnace. This may lead to interference due to absorption by the cyanogen in the spectral region in use. Consequently, either follow the manufacturers recommendation or try both argon and nitrogen when developing a method to determine which gives best results.

Depending on the manufacturer of the instrument the purge gas may or may not flow through the interior of the graphite tube. If it does, the flow rate during the atomization cycle can be critical. Methods in the literature recommend lower flow rates during the atomization cycle in order to increase the retention time of the atoms in the tube. Some instruments allow the user to select this flow rate during programming while others require manual decrease of the flow rates. Some of the methods even call for total interrupt of gas during the appropriate time. However, it should be remembered that the tube lifetime may be shortened when gas interupt is used.

C Ramping

The different manufacturers seem to place different levels of importance on the ability of an instrument to be used in a Ramping Mode. Basically, ramping is the ability of an instrument to be programmed as to the time taken to reach a desired temperature. This ability ranges from complete control through each step, i.e., drying, charing, atomization, to no control at all. Other possibilities include control in only one step and only pre-chosen levels in certain steps.

Ramping becomes valuable when an analyst wishes to go from one temperature to another in longer than the least time possible. This is of particular interest when analyzing samples with a complex make-up such as milk or scum because it will reduce the possibility of spattering. Occasionally the presence of one metal may cause interference in the measurement of a second metal and this may be rectified using the ramping technique.

The analyst should know what is best for his particular sample or vary the ramping time himself to determine whether it will be of use or not. If the analyst believes that ramping is of value, check each manufacturer to ascertain what options are available before purchasing a new instrument or purchase of a retrofit option for an existing furnace-spectrophotometer. Ramping will not be available for all older type furnaces.

D Programming

When a method utilizing the furnace is devised, three steps must be considered.

These are a drying cycle, charing cycle and an atomization cycle. Since the ultimate end of the sample program is dissociation and atomization of the sample, the solvent and all organic matter must be removed. Depending on the sample and the type of instrument, various options are open to the analyst.

1. Dry Cycle
   Normal samples connected with environmental waters would include industrial wastes, municipal wastes and finished potable waters. Consequently, the program for these samples could be complex. The drying cycle is for just that purpose, that is to get rid of the solvent. This cycle of the program would require at least a choice of temperature and holding time. If the ramping option is available, it would be necessary to select a time.

   The temperature to be provided and held by the furnace is usually slightly above the boiling point of the solvent, for aqueous samples about 120 to 125°C. If a ramp is used the temperature should be brought up to this temperature slowly so as to avoid any spattering losses of the sample. Boiling should be avoided and an audible hissing sound from the tube will indicate this is occurring.

   Drying time, that is how long the temperature is to be held by the furnace before proceeding depends upon the volume of sample injected into the tube. A typical time would be about 10 to 15 seconds for a 1 5µ 1 aqueous sample. Samples containing larger amounts of solids may require longer drying times.

   If the ramping option is available for the dry cycle, it can be used to ensure that the sample is evaporated and not boiled away. By inserting a ramping time of several seconds, the temperature is brought up to the desired temperature slowly enough to assure no loss of sample.

2. Charring or Ashing Cycle

   This cycle should be chosen to attempt to get rid of as much of the absorbance due to the matrix of the sample as possible. However, the temperature should not be high enough to allow loss of any of the analyte. Organic materials and materials that are more easily volatilized than the analyte are charred, ashed, or volitilized before the analyte is measured. In order to complete this cycle's program, a temperature and holding time must be chosen and if available, a ramp time.

   The temperature should be high enough to volatilize as completely as possible any interferring sample matrix. If an already existing method is used, this temperature will be included. The analyst should assure himself that this is his optimum temperature by using it as a starting temperature and varying it while checking to see that the absorption peak of the analyte standard is not decreased.

   If a continuous chart recorder trace can be done through the entire program, the pen should return to the baseline after charring before the atomization cycle begins. This will indicate some what the amount of holding time that should be used. However, it is best to be sure that adequate time is being used.

   There are many cases where the optimum charring parameters for elements in complex matrices are very different from parameters for the same elements in aqueous standards. It is important that the analyst consider both the matrix of the solution and the element being analyzed when choosing the charring temperature and holding time.

The use of the ramping technique may be of significant advantage here in this cycle to assist in separating the absorbance peaks for the matrix and analyte. Additional reagents may be added to the graphite tube and a chemical reaction utilized to modify the element changing the temperature at which it will volatilize. This matrix modification will be set down in existing method manuals. An example of this is the use of nickel nitrate in the determination of arsenic.

3. Atomization Cycle

The object of this cycle is to provide sufficient temperature to volatilize the element under investigation quickly and completely. The best way to optimize this temperature is to plot the absorbance vs. atomization temperature and choose the temperature at which a leveling off is noted. The analyst should remember to use the lowest temperature at which acceptable results can be obtained because the higher the temperature used, the shorter the lifetime of the graphite tube.

The holding time should be long enough to obtain the desired absorbance peak and allow the recorder to return to zero before this cycle is ended. The use of a strip chart recorder is recommended to provide visual proof that this is occurring. The recorder should have a quick response time, 0.5 seconds or less for full scale deflection in order to follow the fast peak shaped response of the furnace. The use of the recorder will provide for a permanent record of data as well as to identify any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, insufficient background correction (negative peak), etc.

The other parameter that should be considered during the atomization step, if available on the instrument, is the flow rate of the purge gas. This might be a set rate or no flow at all. The analyst should determine the other parameters and then make runs with standards and determine whether sensitivity is increased sufficiently to warrent its use.

E. Sample Introduction

One additional topic that must be dealt with is sample introduction into the graphite tube. Most manufacturers provide the sample introduction port in the form of a small hole in the tube midway along the tubes length. The sample or standard is introduced into the tube by use of a micro-pipet with disposable tips. These pipets are available from several manufacturers. The technique involved is one which must be practiced in order to deposit the sample in the same area of the tube each time as well as delivering a reproducible amount. Care should be taken to continue to hold down on the pipets plunger until it is removed from the graphite tube to prevent sucking up some of the sample already dispensed. When using these pipets remember that the sample capacity is usually given for aqueous solutions; it is substantially smaller when organics are used.

The reproducibility of data from furnace work is significantly dependent upon the sample dispensing technique. The sample should be added slowly to maintain the least amount of spreading of the liquid along the length of the tube as well as placing of the drop of sample in the same area each time.

Depending on the type of graphite tube being used, spreading is more of a problem. Several manufacturers use threaded or grooved tubes to aid in retaining the sample droplet in the smallest area possible. Aqueous samples do not wet pyrolytic graphite and consequently the sample droplet will stand on the surface of the tube. It is claimed that with non-pyrolytic

graphite the sample soaks into the graphite and does cause reduced sensitivity and reproducibility. However it has been found that non-pyrolytic tubes have given adequate results for most analysis. Organic solvents wet the standard graphite and tend to flow toward the ends of the tube resulting in poor precision or even loss of sample if large volumes are used.

Automatic samplers are available from equipment manufacturers which offer distinct advantages. Since part of the function of this equipment is the introduction of the sample into the graphite tube, the problem of reproducibility caused by pipetting technique is lessened.

F Interferences

The interferences connected with the furnace are different than those found when using the flame. These problems fall under two general categories: background effect and matrix effect.

1. Background effects: In flameless atomic absorption, the major interference occurs when some of the light from the hollow cathode tube, is absorbed or scattered by molecules or solid particles (non-atomic) in the light path. These effects produce an absorption signal which is often very similar to the desired atomic absorption signal, and if the two absorption peaks occur at the same time, a false measurement can result. These molecular or solid particles are produced from the sample matrix.

   The solid particles are generated mostly during the ashing and charring cycles in the form of smoke or vapor. Scattering does not normally create any analytical problems because these materials are normally removed from the graphite tube prior to atomization of the element under investigation.

   Molecular absorption occurs when salts in the sample make-up are vaporized as complete molecules. This can occur during the atomization cycle when the vaporization temperatures for the salts and the analyte are close to each other. This absorption usually can be distinguished from the wanted elemental absorption because the element can only absorb the very narrow spectral line emitted by the hollow cathode lamp. Whereas, the background absorption is less specific and extends over a broader band of wavelength.

2. Background Correction: Background absorption may be corrected by instrumental and technique methods. Instrumental method would be accomplished by difference, i.e., measuring the total absorption and subtracting from it the non-atomic portion. This can be done by:

   a. Compensation using a nearby non-absorbing wavelength or
   b. compensation using a hydrogen-filled lamp.

   There are difficulties with the first way because of the non-reproducible manner in which background absorption signals are produced with furnace techniques.

   Therefore, the second procedure is recommended. This necessitates the purchase of optional equipment for the spectrophotometer. With this procedure simultaneous correction can be obtained at the same wavelength being used to measure the element. Through alternate pulsing, the light emitted by the lamps pass through the same optical path. Basically the element will absorb only from the hollow cathode lamp made from the element while the background absorbs from the hydrogen-filled lamp. Electronic ratioing

of the two beams produce a signal representing only the elemental absorption.

Methods for background correction using variations in the program, i.e., technique methods, can also help to alleviate the problem. Some of these are:

a. Sample dilution or reduced sample size injection
b. Vary program: i.e.
   Increase char time and/or temperature.
   Increase purge gas flow rate.
   Use of ramping techniques.
   Use of alternate absorption wavelengths.

The user should consult the methods manuals of the manufacturer of his instrument for further directions on these steps due to variances of equipment.

3. Matrix Effects: Matrix is used to mean everything that is in the sample other than the element that is to be determined. A matrix component can chemically combine with the element after it has dissociated lowering the ground state atom population within the tube. The formation of less readily dissociated molecular species either before or during atomization affects primarily the rate of dissociation resulting in an apparent decrease in sensitivity.

The presence of excess anions or cations may change the rate of dissociation by causing the element to form more or less volatile compounds that volatize before or after the remaining element thereby lowering the absorption peak height.

When the physical and chemical characteristics of the sample and standards differ considerably, causing a difference in the rate of element volatilization during atomization, it is referred to as matrix interference. These effects can be controlled by matching the components of sample and standard. Since this is not always possible the method of additions should be used. Carbide formation, resulting from the chemical environment of the furnace has been observed with certain elements that form carbides at high temperatures. When this takes place, the metal will be released very slowly from the carbide as atomization continues causing longer atomization times before the signal returns to the baseline. This problem is greatly reduced with the use of pyrolytically coated graphite.

The use of hydrogen gas mixed with the inert purge gas has been recommended for increasing analytical sensitivity and also for suppressing some chemical interferences. Hydrogen acts as a reducing agent and aids in molecular dissociation.

4. Matrix Modification: Another technique which has been used successfully when none of the furnace parameters can be adjusted to a degree where analytical success can be obtained is to modify the matrix. This can be done in two ways, i.e., to modify either the matrix or the analyte. These techniques include:

a. Pre-treatment before analysis: The use of acid digestion or dry ashing to oxidize organic materials of the matrix. Extraction with solvents or chelation-extraction have also been used to concentrate as well as remove the analyte from the bulk of the background causing materials.

b. Modification in the furnace: Chemical reactions may be carried out in the graphite tube itself. The object is to reduce the interference caused by material in the sample. This can be done by adding chemicals which will reduce the interference caused by the matrix by

a) reducing volatility of the analyte or b) increasing the volatility of the matrix, in order to facilitate more effective removal of the matrix prior to atomization. Directions on the use of these modification techniques are usually a part of the methods writeup. The manual for "Methods for Chemical Analysis of Water and Wastes" by the EPA includes such procedures which can be used.

5. Contamination: Contamination of the sample or standard can be a major source of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned by washing with detergent, rinsed with tap water, rinsed with 1:1 hydrochloric acid, rinsed with tap water and finally with deionized distilled water in that order. The disposable micro pipet tips have been known to be contaminated and should be acid soaked with 1:5 nitric acid and rinsed thoroughly with tap and deionized water. The use of research grade tips can greatly reduce this problem. It is important that special attention be given to reagent blanks in both analysis and the correction of analytical results. Lastly, pyrolytic graphite, because of production and handling processes, can become contaminated. Five to ten high temperature burns may be required to clean the tube before use.

6. Verification of Interferences: With non-flame techniques the compositions of the sample matrix can have a major effect upon the analysis. These effects must be determined and taken into consideration in the analysis of each type of matrix encountered. To help verify the absence of matrix or chemical interference, use the following procedure set down in the EPA methods manual.

Withdraw two equally sized aliquots from the sample. To one of the aliquots add a known amount of analyte and dilute both aliquots to some pre-determined volume. This dilution volume should be based on a preliminary analysis of the undiluted sample. Preferably, the dilutions should be one volume of sample to four volumes of dilutant. Keeping in mind the optimum concentrations range of the analysis. Under no circumstances should the dilution be less than equal volumes. The diluted aliquots should then be analyzed and the unspiked results compared to the preliminary determination. Agreement of the results within $\pm$ 10%. indicates the absences of interferences. Comparison of the actual signal from the spike to the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis. Those samples which indicate the presence of interference should be treated in one or more of the ways mentioned, they are, dilution, matrix modification and the use of standard additions.

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This outline was prepared by John D. Pfaff, Chemist, National Training and Operational Technology Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Atomic Absorption, Furnace, Water Pollution, and Water Supply.

PRINCIPLES OF ABSORPTION SPECTROSCOPY

I INTRODUCTION

In any system employing principles of absorption spectroscopy, there are three basic components.

A SOURCE of Radiant Energy

B MEDIUM (Sample) which absorbs Radiant Energy

C DETECTOR to measure the Radiant Energy transmitted by the Sample

Figure 1. Basic Components of Absorption Spectroscopy System

II RADIANT ENERGY

A Wave Nature

1 The various forms of radiant energy have been arranged in a single schematic diagram referred to as the electromagnetic spectrum (see Figure 2). All of the energies which make up this spectrum may be represented graphically as waves. All waves move through space (and for most purposes air) at a constant velocity, 3×10^{10} cm/sec.

2 Three variable characteristics of individual waves serve to differentiate each from all other waves in the spectrum.

a The Wave Length

λ - The linear distance between the crests of two adjacent waves. (Units: distance/wave.)

b The Frequency

ν - The number of waves which pass a given point in a unit of time. (Units: waves/time unit.)

c The Wave Number

$\bar{\nu}$ - The number of waves which occur in a given linear distance. (Units: waves/distance unit.)

2 It is evident that more waves of short wavelength will "fit" into a given linear distance than would waves of a greater wavelength. Thus, waves having short wavelengths will have higher wave numbers. Mathematically, wave length is the reciprocal of wave number, if the same units of linear measurement are used in each expression. Since the velocity of all waves is equal and constant, it is also apparent that a greater number of waves of short wavelength can pass a given point in a unit of time than waves having a longer wavelength.

B Particle Nature

Planck conducted certain experiments which indicated that light has a particle as well as a wave nature. Energy rays can be said to consist of particles with a definite amount of energy. These particles or packets are referred to as photons or quanta. The energy (E) of each minute packet is given by Planck's equation.

$E = h\nu$ (5)

Where E = Radiant Energy in ergs

h = Planck's proportionality constant (6.6×10^{-27} erg sec.)

ν = Frequency in waves per second

Thus, it can be seen that the energy of a given photon is directly proportional to the frequency of the given Radiant Energy.

III ABSORPTION OF ENERGY BY ATOMS AND MOLECULES

A Absorption of energies of given frequencies by atoms and molecules can be used as a basis for their qualitative identification. Absorption spectroscopy is based on the principle that certain displacements of electrons or atoms within a molecule are permissible according to the quantum theory. When radiant energy of the same energy required to bring about this permissible change is supplied to the molecule, the change occurs and energy is absorbed.

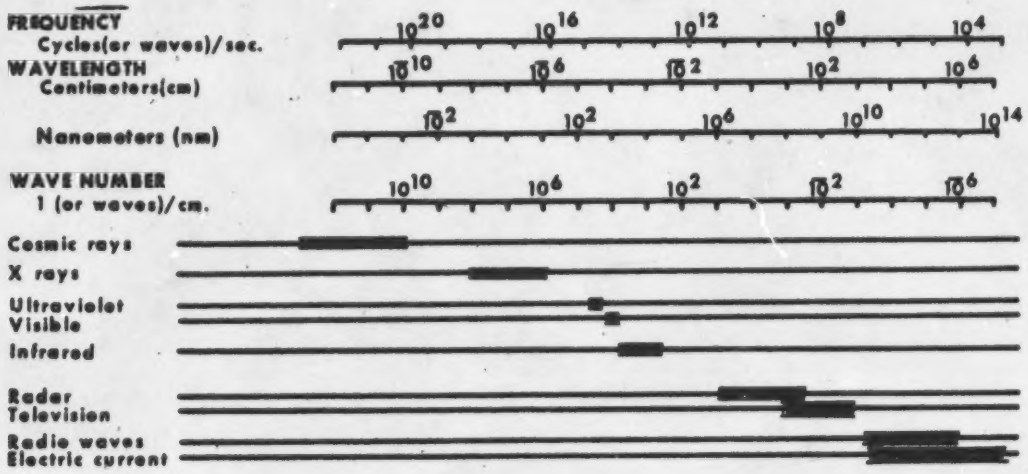
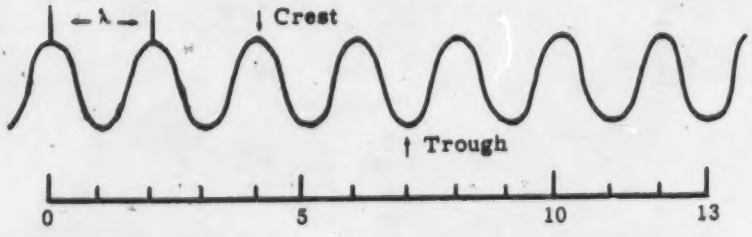


FIGURE 2



(1)	WAVE LENGTH	×	FREQUENCY	=	CONSTANT	
(2)	λ	×	ν	=	c	
(3)	$\frac{\text{distance}}{\text{wave}}$	×	$\frac{\text{waves}}{\text{time}}$	=	$\frac{\text{distance}}{\text{time}}$	= VELOCITY
(4)	λ (cm/wave)	×	ν (waves/sec)	=	C = (3×10^{10} cm/sec)	

Figure 3. Relationship of Wave Length and Frequency

8-2

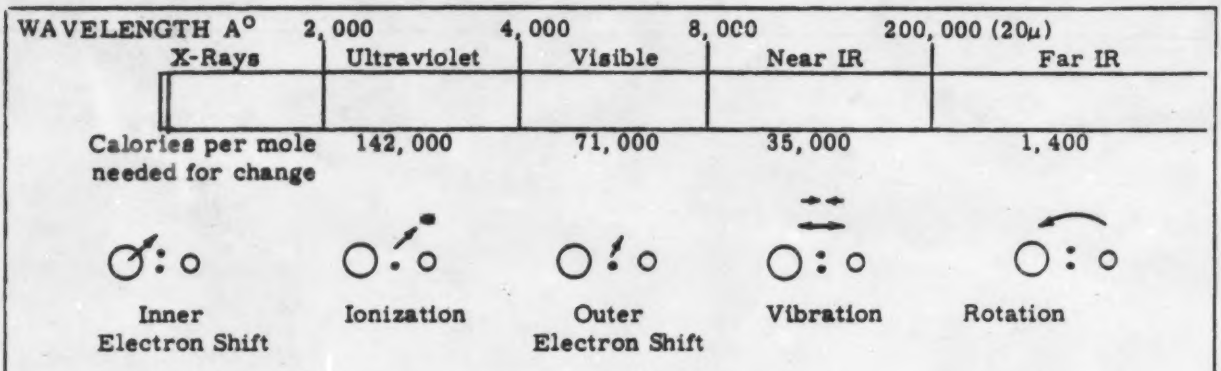


Figure 4. Electromagnetic Spectrum Showing Energy Ranges and Corresponding Electronic, Vibrational and Rotational Motions

1 Displacement of electrons is a permissible change which can occur when energy of ultraviolet and visible frequencies strikes certain atoms and molecules.

a Inner electron shift

Electrons located in the inner orbit of an atom may, when the proper frequency of radiant energy is available, shift to an orbit farther removed from the nucleus. This shift represents a change from a lower energy to a higher one. If this new position is unstable, the electron may revert to some position nearer the nucleus; the energy which was gained may then be emitted from the atom as part of its emission spectrum. The number of energy changes possible within an atom is a function of the number of electrons and the number of changes each may enter. Each possible change gives rise to a new spectral frequency. Since the frequency of radiation needed to accomplish such changes is of a high order of magnitude, the energy used is considerable in quantity.

Molecular aggregations often disintegrate in such circumstances; thus, these higher frequencies are used mainly for work with elements or very stable compounds.

b Ionization

Under a specific frequency of radiation, an electron may be physically separated from its parent atom. This process has been termed ionization. A change of energy level of this magnitude requires less energy than the inner electron shift. Such changes are characteristic of those of the rare earths, inorganic ions, transition elements and many organic compounds under frequencies within the ultraviolet range.

c Outer electron shift

The various orbital electrons in an atom may vary in the amount of energy required to shift them outwardly from the nucleus. For example, it requires less energy to shift an electron from a position more distant than it does to shift an electron outwardly from the inner orbit. Outer electron shifts occur readily in colored organic molecules for which

electronic transitions are made easier by the presence of chromophore groups which participate in resonance. Thus, the excitation of the delocalized outer electrons (pi electrons) is relatively easy and requires energy in the visible range.

2 Vibration of atoms within molecules is a permissible change which can occur when energy of near infrared frequency strikes certain organic molecules.

The atoms within a molecule are held together by attractive bonding forces. Atoms within a molecule are constantly moving toward and away from other atoms, but for purposes of theory can be said to have a certain "average" position.

The change in position of an atom in relation to another atom is called vibration. The mechanics of vibration require energy; the manner and rate of vibration of the atoms depend upon frequencies of electromagnetic radiation which strikes them. Therefore, a specific part of a molecule may absorb significant quantities of certain spectral frequencies. Such absorption will be reflected in the absorption spectrum of the compound. The energy requirements for this type of energy change are of a lower order of magnitude than those above; therefore, we would expect that the frequency required would be lower and the wave length longer. Such changes occur in organic compounds under infrared radiation.

3 Rotation of molecules is a permissible change which can occur when energy of far infrared frequency strikes certain organic molecules.

A molecule rotates around its symmetrical center. The manner and rate of rotation again depends upon the energy supplied to it.

Specific spectral frequencies of electromagnetic radiation can be employed to increase the rate of rotation. The used radiation is, in effect, absorbed and reflected in the absorption spectrum.

Organic molecules utilize infrared radiation while varying their rate and manner of rotation.

B The Lambert-Beer Law provides the basis for quantitative analysis by absorption spectroscopy. It is a combination of the Bouguer (or Bouguer-Lambert) and Beer Laws.

1 Bouguer (or Bouguer-Lambert) Law

When a beam of monochromatic radiation passes through an absorbing medium, each infinitesimally small layer of the medium decreases the intensity of the beam by a constant fraction.

Mathematically:

$$\frac{-dI}{I} = k\ db \qquad (6)$$

On integration and converting base e to base 10 logarithms,

$$\log \frac{I_o}{I} = A = Kb \qquad (7)$$

-dI = increment by which incident monochromatic radiation is decreased (or absorbed) by the medium.

I = intensity of the radiation emerging from the absorbing medium.

k = proportionality constant whose value depends on the wave length and the nature of the medium; i.e., the solvent used if the absorbing medium is a solution, and the temperature.

db = increment thickness of the absorbing medium.

I_o = radiation entering the medium.

$\log \frac{I_o}{I}$ = A = absorbance (optical density)

K = 2.303 k

b = length of radiation passing through the medium (i.e., the width of the cell, generally express in cm.)

2 Beer's Law

Each molecule of an absorbing medium absorbs the same fraction of radiation incident upon it regardless of concentration.

Mathematically:

$$\frac{-dI}{I} = k' \, dc \qquad (8)$$

On integration and converting base e to base 10 logarithms,

$$\log \frac{I_o}{I} = K' c \qquad (9)$$

k' = a proportionality constant whose value is governed by the same factors which determine the value of k.

dc = increment concentration of the absorbing medium.

K' = 2.303 k'

c = concentration of the absorbing medium (in the case of a solution c is generally expressed in moles/liter.)

3 Lambert-Beer Law

$$A = \log \frac{I_o}{D} = e \, b \, c \qquad (10)$$

e = a constant obtained by combining K plus K'. When b is expressed in cm and c in moles/liter, e is called the molar absorptivity.

4 The term transmittance is sometimes used to express how much radiation has been absorbed by a medium.

$$\text{Transmittance (T)} = \frac{I}{I_o} \qquad (11)$$

$$\text{\% Transmittance (\%T)} = \frac{I}{I_o} 100 \qquad (12)$$

The relationship between absorbance and transmittance is given by the expression:

$$A = \log \frac{I}{T}$$

5 The application of the Lambert-Beer Law to a problem involving quantitative analysis is made by the use of a calibration curve (or graph). See Figure 5.

Several standard solutions containing known concentrations of the material under analysis are "read" in the spectrophotometer. Figure 5 is prepared by graphing concentrations vs. corresponding absorbance readings.

If a straight line is obtained, the material is said to follow Beer's Law in the concentration range involved. The absorbance of the sample is then "read" and the corresponding concentration obtained from the calibration curve.

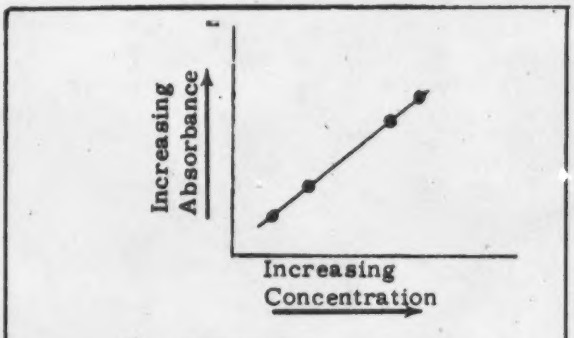


Figure 5.

ACKNOWLEDGMENT:

This outline contains certain portions from a previous outline by Betty Ann Punghorst, former Chemist, National Training Center.

RANGE	SOURCE OF RADIANT ENERGY	ABSORPTION BY SAMPLE		DETECTION OF RADIANT ENERGY TRANSMITTED
		CHEMICAL NATURE OF SAMPLE	TYPE OF SAMPLE CELL USED	
Ultraviolet	Hydrogen Arc	Inorganic ions and Organic Molecules	Quartz Fluorite	Photoelectric Cells Photographic Plates
Visible	Incandescent Tungsten Bulb	Colored Inorganic and Organic Molecules	Glass	Eye Photographic Plates Photoelectric Cells
Infrared	Nernst Glower Globar Lamp	Organic Molecules	Sodium Chloride or Potassium Bromide	Thermocouple

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This outline was prepared by C. R. Feldmann, National Training Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Chemical Analysis, Water Tests, Spectroscopy, Spectrophotometry

FLAME PHOTOMETRY

I PRELIMINARY

Flame photometry is the art and science of applying thermal energy (heat) to elements in order to effect orbital shifts which produce measurable characteristic radiations. The color of the emission and the intensity of brightness of emission permit both qualitative and quantitative identification.

The application of a very hot flame (2000° C or more) produces excitation of the element, caused by the raising of an electron to a higher energy level and is followed by the loss of a small amount of energy in the form of radiant energy as the electron falls back into its original position or to a lower energy level.

II INSTRUMENTATION

The six essential parts of a flame photometer are: pressure regulators and flow meters for the fuel gases, atomizer, burner, optical system, photosensitive detector and an instrument for indicating or recording output of the detector. These components are schematically shown in Figure 1.

A Atomizer and Burner

Numerous variations in atomizer and burner designs have been used. Figure 2 depicts the integral aspirator-burner used in Beckman instruments. The sample is introduced through the innermost concentric tube, a vertical

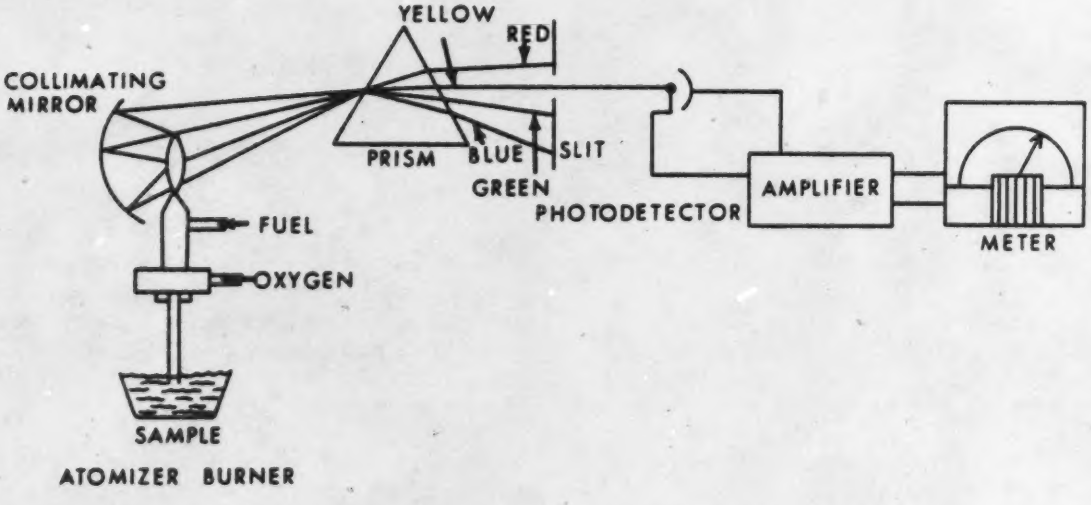


FIGURE 1. SIMPLIFIED DIAGRAM OF A FLAME PHOTOMETER

palladium capillary. A concentric channel provides oxygen, and its tip is constricted to form an orifice. Oxygen is passed from this orifice causing the sample solution to be drawn up to the tip of the inner capillary. There, the liquid is sheared off and dispersed into droplets. All droplets are introduced directly into flame, with a sample consumption of 1 - 2 ml per minute.

The main requirement of the burner is production of a steady flame when supplied with fuel and oxygen or air at constant pressures. In the Beckman aspirator-burner, a concentric channel provides oxygen to operate the atomizer and the flame. The additional concentric channel provides fuel for the flame.

B Optical System, Photosensitive Detector and Amplifier

The optical system must collect the light from the steadiest part of the flame, render it monochromatic with a prism, grating or filters, and then focus it onto the photosensitive surface of the detector. Use of filter photometers is least desirable due to their limited resolution. Flame spectrophotometers improve application as they will separate emissions in a mixture of metals, such as manganese lines at 403.3 nm and the potassium lines at 404.6 nm Placement of a concave mirror behind the flame so that the flame is at the center of the curvature increases intensity of flame emission by a factor of 2.

Any photosensitive device may be used in a flame photometer. The detector must have a response in the portion of the spectrum to be used and have good sensitivity. The photomultiplier tube is the preferred detector for flame spectrophotometers.

The amplifier increases the signal from the phototube and improves resolution between close spectral lines. It also permits identification of elements present in samples when the concentration is very small.

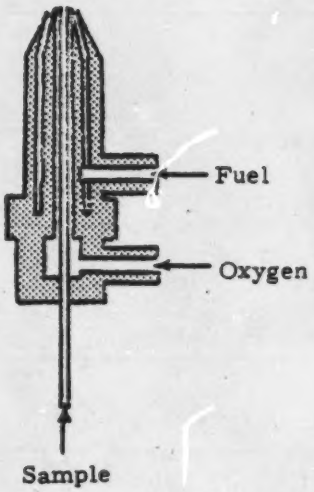


Figure 2. DETAILED DIAGRAM OF BURNER-ATOMIZER

III APPLICATIONS OF FLAME PHOTOMETRY TO WATER ANALYSES

Measurement of sodium and potassium in the past has been confined to complex, tedious and time-consuming gravimetric procedures. The flame technique enables the analyst to perform these determinations in a matter of seconds. If these metals alone were the only elements capable of measurement by flame photometry the use of the instrument could still be justified in a great many laboratories.

Other cations which may be detected and measured in waters and waste materials are calcium, magnesium, lithium, copper, and others. Table 1 includes those elements which may be measured with commercially available equipment, including ultra-violet and photomultiplier accessories.

Table 1 does not include wavebands which occur in the infrared spectrum. Sodium, for example, has an emission band at 819 nm which is not detectable with the common instruments.

Many other metals, including the rare earths, can be measured using the flame technique but they are not included in the table because

Table 1

	Wavelength	Approximate Sensitivity mg/l		Wavelength	Approximate Sensitivity mg/l
Aluminum	484.2	2	Lead	405	2
	467.2	3		368?	2
	396.2	4		364?	3
Barium	553.6	0.3	Lithium	670.8	0.002
	493	0.4			
			Magnesium	371	0.1
Beryllium	471	25		383?	0.1
	510	100		285.2	0.2
Boron	548	1	Manganese	403	0.01
	521	2		279*	1
	495	3		561	2
Cadmium	326.1?	2	Mercury	235.7*	10
	228.8*	40			
			Potassium	766.5	0.001
Calcium	422.7	0.003		404.6	0.2
	622	0.004		344.7?	3
	554	0.01			
			Silver	338.3?	0.05
Chromium	425.4	0.1		328.1?	0.1
	360?	0.1			
	520	0.1	Sodium	589.3	0.002
				330.3?	1
Copper	324?	0.01			
	327?	0.01	Strontium	460.7	0.02
				681	0.01
Iron	372	0.2		407.8	0.5
	386	0.2			
	373	0.3	Zinc	213.9*	500
				500	200

* = Ultra-violet spectrum

? = Doubtful detection in visible spectrum

the necessity for their measurement in water is a rare occurrence.

IV INTERFERENCES

A Spectroscopic Interferences

Energy at other wave lengths or from other elements than those intended to be measured may reach the detector. This problem is related to the resolution of the instrument and slit widths used.

Many of the instrumental difficulties are related to reproducibility of the flame. The quality and composition of the fuel affect the constancy and temperature of the flame which in turn influences the energy of emission. Likewise, slight variations in fuel pressures and ratios affect the reproducibility of the flame with reference to shape, temperature, background, rate of sample consumption, etc. In some cases, the temperature of the flame is the limiting factor in determining the presence of a metal. (The alkaline earth metals emit radiations at "low" temperatures, whereas other metals require very "hot" flames.)

Table 2 indicates temperatures obtainable with different fuel-oxidant mixtures.

Table 2.
Approximate Temperatures of Fuel-Oxidant Mixtures for Flame Photometer Use

Fuel-Oxidant	Approximate Temp. °C
Hydrogen - air	2100
Hydrogen - oxygen	2700 - 2800
Acetylene - oxygen	3100
Acetylene - air *	2000 - 2200
Propane - oxygen	2700 - 2800
Illuminating gas - oxygen	2800
Cyanogen - oxygen **	4900

* Undesirable because of carbon deposits.
** Used in research problems.

Emission reading of spectral lines always includes any contribution from the flame background emission on which the line is superimposed. When the photometer includes a monochromator, it is possible to read the background radiation in the presence of the test element. First, the line + background intensity is measured in the normal manner at the peak or crest of the band system. Next, the wave length dial is rotated slowly until emission readings decrease to a minimum at a wave length located off to one side or the other of the emission line or band. It is usually preferable to read the background at a lower wave length than the peak. Background reading is subtracted from the line + background reading.

Products of combustion may affect the characteristics of the flame or may affect the optical system by fogging or coating of lenses and mirrors.

B Factors Related to the Composition of the Sample

An element may be self-absorbing -- a phenomenon in which the energy of excitation is not proportional to the concentration of the element. As previously discussed, exictation is followed by loss of energy in the form of radiation as the electron falls back to its original position or to a lower energy level. During passage of radiant energy through the outer fringes of the flame, this energy is subject to absorption through collision with atoms of its own kind present in the ground energy level. Absorption of radiant energy weakens the strength of the spectrum line. Using the emission line at 589 nm for sodium, Figure 3 indicates that the line ceases to be linear at 13 mg/l. As the sodium concentration increases, the self-absorption effects become more pronounced. Sample dilution to permit reading on linear portion of the curve is often practiced.

Two or more elements present in the sample may produce radiant energy at

the same, or near the same wavelength. For instance, calcium at 423 nm and chromium at 425 nm could interfere with each other by additive effect. The correction may be to dilute out the unwanted metal or measure one of the emissions at a different wavelength.

The emission energy of one element may be enhanced or depressed by energies from other elements. This phenomenon (radiation interference) occurs when one element causes another to modify its actual emission intensity in either a negative or positive manner. Correction is obtained by dilution or by controlled interference addition.

Other types of difficulties encountered are too numerous to list here. In general, they may be overcome by improved instruments (high resolution, narrower slit openings, optics, flame adjustment) or possibly by special techniques.

Some inexpensive instruments, designed for limited use, may employ illuminating gas with air or propane with air as a matter of economy or convenience.

STANDARD CURVE FOR SODIUM

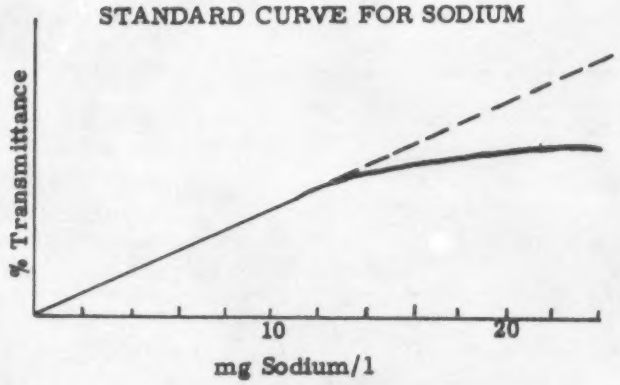


Figure 3

V TECHNIQUES

The following techniques are intended to serve as examples of current procedures in use for routine samples and for special samples where corrective procedures are indicated.

A Emission Intensity vs. Concentration

This is the classical procedure in flame photometry. Solutions (standards) containing known concentrations of test elements are compared with an unknown sample. This technique is applicable only when no interference is present.

B Radiation Buffers

For measurements of alkaline earth metals (sodium, potassium, calcium, magnesium) radiation buffers are prepared as solutions saturated with regard to each metal, respectively. A potassium buffer, for example, is prepared by saturating distilled water with sodium, calcium, and magnesium chloride. A calcium buffer in turn is saturated with sodium, potassium and magnesium chloride.

C Preparation of Radiation Buffers

For a sodium measurement, the buffer solution is added equally to samples and standards so that the interferences are alike for all readings, thereby cancelling each other (see Table 3).

D Instrument Improvement

Potassium emits energy bands at 766, 405, and 345 nm. The bands are at opposite ends of the spectrum and the 405 and 345 bands are not usable in the visible spectrum. The 766 line also loses sensitivity because of its proximity to the infrared region. Use of a red sensitive phototube or photomultiplier, however, permits measurement with an ordinary instrument at concentrations as low as 0.1 mg/l, or less. This approach is applicable to other elements also.

E Standard Addition

Equal volumes of the sample are added to a series of standard solutions containing different known quantities of test element, all diluted to the same volume (see Table 4). Emission intensities of the resulting solutions are then determined at the wavelength of maximum emission and at a suitable point on the flame background. After subtracting the background emission, the resulting net emissions are plotted linearly against the concentration of the increments of the standard solutions that were mixed with the unknown. The percent transmission of the mixture containing unknown sample and zero standard (distilled water) is doubled and the concentration corresponding to this point on the graph will be the concentration of the undiluted unknown sample. This can be explained algebraically in conjunction with Figure 4.

F Internal-Standard Method

The method consists of adding to each sample and standard a fixed quantity of internal standard element. The element must be one not already present in the sample. Lithium is usually the internal standard used. This method is most convenient when using instruments having dual detectors. The emission intensities of standards and samples are read simultaneously or successively depending upon instrumentation.

G Separation of Interferences

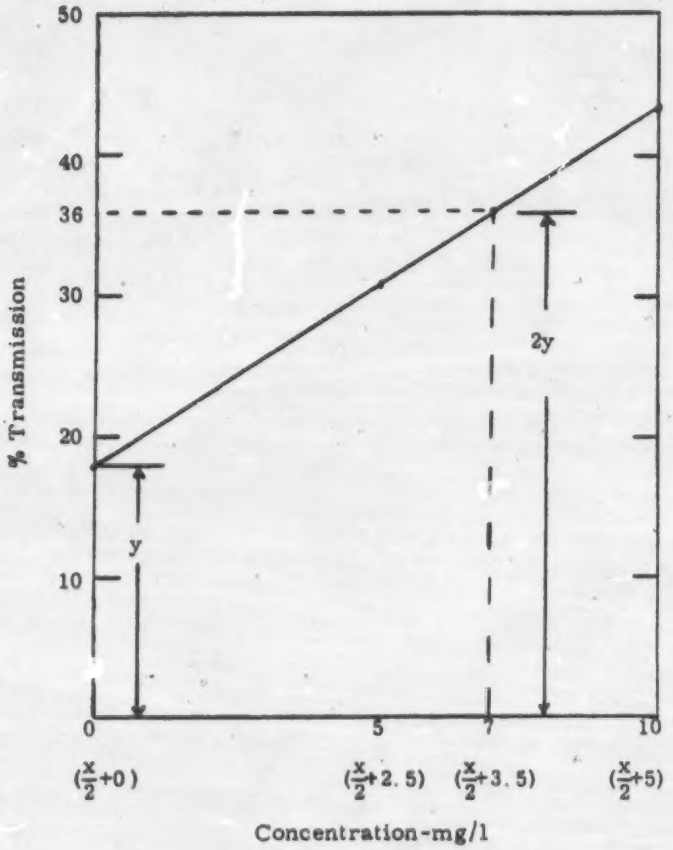
In cases where certain elements interfere, they may be physically removed, or the interference may be "blocked out" by reading the emission at different wavelengths. To measure lithium, for example, calcium, barium, and strontium are precipitated as carbonates of the metals. The lithium is retained in the filtrate and measured at a wavelength of 671 nm.

	NaCl	KCl	$CaCl_2$	$MgCl_2$
Sodium Buffer	-	+	+	+
Potassium Buffer	+	-	+	+
Calcium Buffer	+	+	-	+
Magnesium Buffer	+	+	+	-

Table 3

Conc. of standards	0.0 mg/l	5.0 mg/l	10.0 mg/l
Volume of standard added to sample	10.0 ml	10.0 ml	10.0 ml
Volume of sample used	10.0 ml	10.0 ml	10.0 ml
Concentration of element in each portion of mixture	$\frac{x}{2}$ + 0 mg/l	$\frac{x}{2}$ + 2.5 mg/l	$\frac{x}{2}$ + 5 mg/l

Table 4



Let x = concentration of element in unknown sample.

Then Y = % transmission of an equal mixture of unknown sample and zero standard, or

$$Y = \frac{x}{2} + \frac{0}{2}$$ which simplifies to $2Y = x$

$\therefore$ $2Y = \frac{x}{2} + 3.5$ (from the example in Figure 4)

by substitution, $x = \frac{x}{2} + 3.5$

$$\frac{x}{2} = 3.5$$

$$x = 7 \text{ mg/l}$$

Figure 4

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This outline was prepared by R. C. Kroner, Chief, Physical and Chemical Methods, Analytical Quality Control Laboratory, NERC, EPA, Cincinnati, OH 45268.

Descriptors: Chemical Analysis, Water Tests, Flame Photometry, Spectrophotometry, Spectroscopy

FLAMELESS MERCURY FOR ANALYTICAL METHODS FOR TRACE METALS

DETERMINATION OF MERCURY

I INTRODUCTION

There are many forms of mercury, some more toxic to humans than others. Although metallic mercury and its inorganic, alkoxyalkyl, and aryl compounds can have detrimental effects on man and other animals, it has become clear that methylmercury poses a particularly serious problem. It appears that mercury enters the food chain as methyl mercury after conversion by microorganisms in the silt of waterways.

Sources of mercury in industrial and agricultural countries fall into the following categories: 1) chlor-alkali plants, 2) industrial processes involving the use of mercurial catalysts, 3) slimicides, used primarily in the paper-pulp industry, 4) seed treatment, 5) burning of fossil fuels, 6) natural occurence from geological formations, and 7) miscellaneous sources.

Early in 1970 fish in Lake St. Clair above Detroit were shown to contain hazardous levels of methyl mercury. However, even before this other countries such as Japan were having serious problems with mercury poisoning. "Minamata Disease" or methyl mercury poisoning due to ingestion of contaminated fish occurred in a village near the Minamata Bay, Japan, from 1953 through the 1960's, and affected at least 121 children and adults. Consequently, the finding of high levels of methyl mercury in Lake St. Clair caused the United States and Canada to ban fishing in the lake.

A study was carried out by the Office of Water Supply during 1971 analyzing 698 samples of raw and finished waters collected from 273 communities. Of these 273 communities, 261 showed no detectable quantities or concentration of less than 0.001 ppm. In eleven of the communities the mercury concentration ranged from 0.0010 to 0.0048 ppm.

After the discovery of mercury contamination in fish, the importance of the mercury content of waters can be seen by the decreasing allowable limits. The 1962 edition of the Public Health Service Drinking Water Standards did not list a limit for mercury. However, in 1970 a tentative standard of 0.005 mg/l limit was proposed. Recently, March 1975, the Interim Primary Drinking Water Standards proposed a limit of 0.002 mg/l.

II METHODS

A Dithizone

Until about 1964 the method of choice for analysis of mercury was the dithizone method. This method utilized a colorimetric determination of the dithizone complex with mercury. The method has been characterized as relatively insensitive and requiring excessive amounts of sample when levels of mercury are low. The analyst must have experience in order to obtain meaningful results due to the possibility of loss of volatile forms of mercury during a hot acid digestion procedure. The method covered the range of 0.005 mg/l to .035 mg/l.

B Emission Spectroscopy

The emission spectrophotometric determination of mercury was also carried out. However, the cost of the instrument made this method considerably more expensive than the dithizone method. The detection limit fell in the range of about 5 mg/l so no increase in sensitivity could be obtained.

C Atomic Absorption

The detection limit by direct aspiration of a sample into the instrument was claimed to be 0.5 mg/l. However, in actual practice the limit was closer to 5.0 mg/l. A concentration step before aspiration by

chelation with ammonium pyrrolidine dithiocarbamate and extraction with methyl isobutyl ketone, reduced the detection limit to about 0.2 mg/l. Additional sensitivity was claimed by using the sample boat which evaporated one milliliter of sample in a boat like device followed by ignition of boat in the flame. This helped reduce the detection limit to around 0.02 mg/l but here again in actual practice the sensitivity was probably less.

D Gas Chromatography

A swedish method utilized an electron capture detector to detect materials at a sensitivity approaching 0.001 mg/l in favorable cases. This procedure was good for the organic forms of mercury contamination such as methyl mercury, ethyl mercury and methoxy ethyl mercury, and phenyl mercury. Dimethyl mercury and the inorganic forms of mercury gave no response in this procedure.

E Flameless Atomic Absorption

It had long been known that the metallic mercury vapor absorbed energy at 2537 A. However, it was not until 1968 that a method was practical. This method converts all forms of mercury present in the sample to the metallic form. Therefore, the results in this method are only for total mercury since there is no differentiation. The detection limit for mercury was lowered to a point that made adoption of low standards analytically practicable. The detection limit for mercury by the flameless method was reduced to 0.0002 mg/l.

This procedure has become the standard analytical procedure for the analysis of mercury. Both the National Pollution Discharge Elimination System's analytical methods and the methods recommended to meet the Primary Drinking Water Standards recommend the flameless atomic absorption technique.

III FLAMELESS METHOD

A Chemistry

The procedure covered here is the procedure recommended in the Environmental Protection Agency's manual of "Methods for Chemical Analysis of Water and Wastes." The method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

In addition to inorganic forms of mercury, organic mercurials may also be present in a sample. These organo-mercury compounds will not respond to the falmeless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercury compounds, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the potassium permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. The range of the method may be varied through instrument and/or recorder expansion. Using a 100 ml sample, a detection limit of 0.2 μg Hg/l can be achieved; concentrations below this level should be reported as < 0.2.

Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from

spiked samples. Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml). During the oxidation step chlorides are converted to free chlorine which will also absorb energy at 253 nm. Care must be taken to assure that the free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of the hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the aeration bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.

Interference from certain volatile organic materials which will absorb at this wavelength (253 nm) is also possible. A preliminary run without reagents should determine if this type of interference is present. If an interference is found to be present, the sample should be analyzed both by using the regular procedure and again under oxidizing conditions only, that is without the reducing reagents. The true mercury value can then be obtained by subtracting the two values.

The chemical procedure involves obtaining a sample of at least 100 ml. Until more conclusive data are obtained, preservation of samples can be accomplished by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection. The 100 ml sample is placed in a 300 ml BOD bottle. Add 5 ml of concentrated sulfuric acid and 2.5 ml of concentrated nitric acid, mixing after each addition. Add 15 ml of potassium permanganate solution (5% solution) to each bottle. For sewage samples additional potassium permanganate may be required. Shake and add additional amounts of potassium permanganate, if necessary, until the purple color exists for at least 15 minutes. Add 8 ml of potassium persulfate (5% solution) to each bottle and heat for two hours in a water bath at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (12 grams of each diluted to 100 ml) to reduce the excess potassium permanganate. Allow to stand at least 30 seconds.

Up to this point all samples and standards being run can be treated in a group. However, the final step should be done just before the BOD bottle containing the solution is attached to the instrument. This is to reduce the possibility of loss of any mercury vapor. The final step in the procedure is to add 5 ml of stannous sulfate (25 g diluted to 250 ml with 0.5 N sulfuric acid). After the BOD bottle has been attached the sample is allowed to stand quietly without manual agitation. The circulating pump is allowed to run continuously. The absorbance will increase and reach maximum within one minute. As soon as the indicating device (meter or recorder) levels off the reading is taken and the mercury vapor trapped.

B Aeration Gas Flow Path

Once the mercury is reduced to metallic mercury by the stannous sulfate, the metallic vapor begins to escape from the solution. In order to quantitatively drive off all the vapor a pump is used to push air into the solution through an aeration device such as a glass frit of coarse porosity. The air acts as a carrier gas for the vapor. An aeration device may be constructed as shown in Figure 1.

Any peristaltic pump capable of delivering one liter of air per minute may be used. The pump should be checked occasionally via a rotometer to assure that sufficient flow is being provided.

The flow path of the procedure can be set up in two ways, in an open mode and a closed mode. The closed mode recirculates the mercury vapor through the entire flow path, including the absorption cell, until a manual valve shunts the vapors to a trap. The open mode allows the vapors to pass only one time through the absorption tube and from there it goes to a trap.

There are several pieces of equipment involved in the flow path that are common to both modes. The aeration bottle has been mentioned before, next in line should come a desiccant (of magnesium perchlorate) to adsorb water vapors in order to prevent these from condensing in the absorption tube. If a conventional atomic absorption

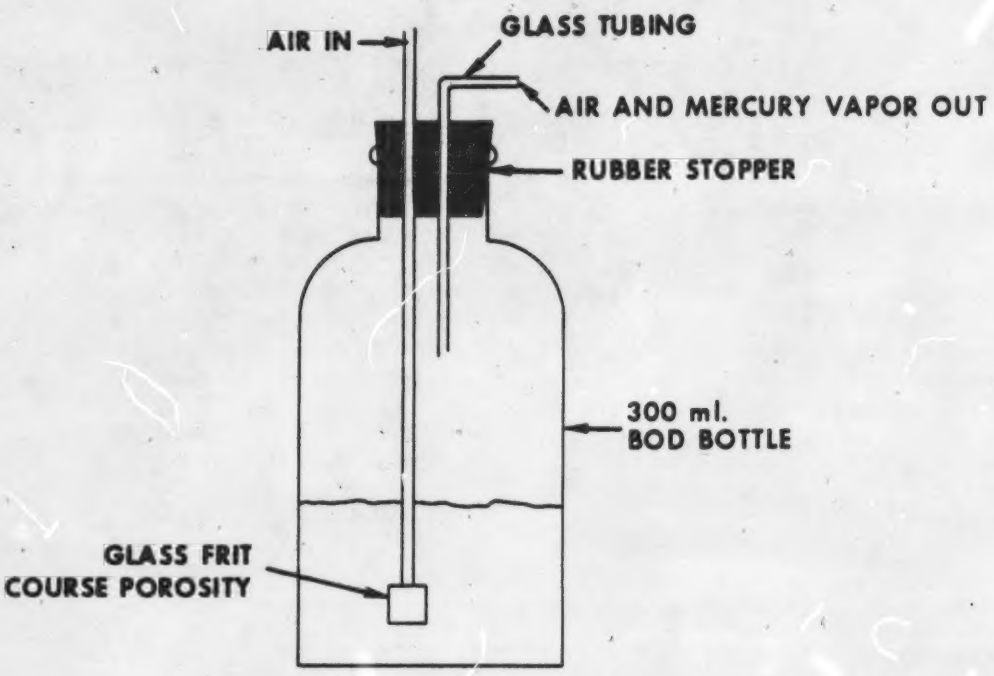


Figure 1. Aeration Bottle

spectrophotometer is being used, the desiccant can be replaced with a small 60 watt lamp. This is positioned to shine on the tube itself to raise the temperature inside the tube thus preventing condensation. Next in the flow path after the desiccant would come the absorption cell, or instrument.

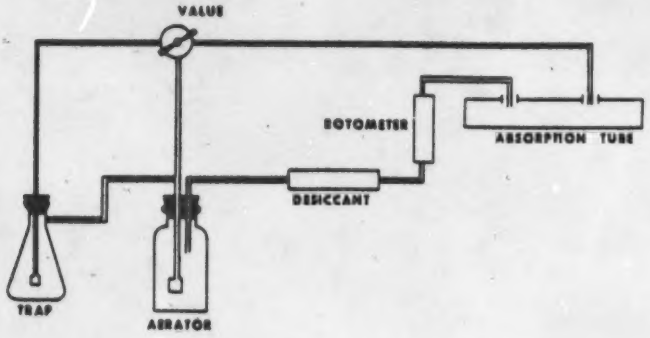
In the open mode a trap for the mercury vapors would follow the absorption tube. In the closed mode a valve would follow. The position of each of these pieces can be seen in Figure 2.

The absorption tube or cell can be a standard spectrophotometer cell that is 10 cm long and having quartz end windows. Suitable cells may be constructed from plexiglass tubing 1 inch outside diameter and 4½ inches long. The ends are ground perpendicular to the longitudinal axis and quartz windows 1 inch in diameter and one sixteenth of an inch thick are cemented in place. Gas inlet and outlet ports (also of plexiglass but ¼ inch outside diameter) are attached approximately ½ inch from each end.

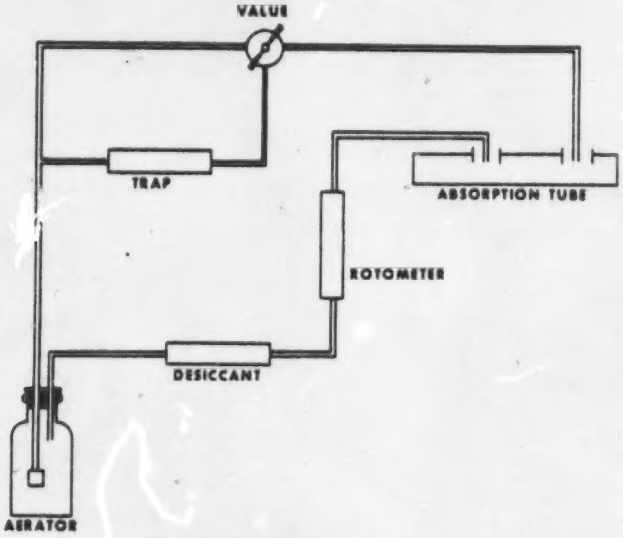
C Instrumentation

Any atomic absorption spectrophotometer having an open sample presentation area in which the absorption tube can be mounted is suitable. The absorption tube is strapped to a burner for support and aligned in the beam by use of two 2 x 2 cards. One inch diameter holes are cut in the center of each card; the cards are placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

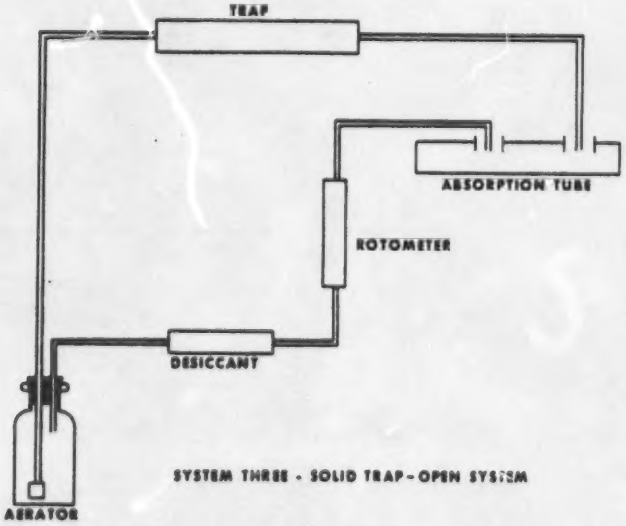
There are available on the market instruments designed specifically for the determination of mercury by the flameless atomic absorption method. Usually they are complete and contain the absorption tube and pump inside the instrument. The main advantage of these instruments is that they are considerably cheaper than an atomic absorption instrument. However, their chief disadvantage lies in the fact that they can be used only for mercury while an atomic absorption instrument with some additional equipment (lamps) can be used for about 40 metals.



SYSTEM ONE- LIQUID TRAP CLOSED SYSTEM



SYSTEM TWO - SOLID TRAP CLOSED SYSTEM



SYSTEM THREE - SOLID TRAP - OPEN SYSTEM

Figure 3. Flow Systems

There is also available an automated method which utilized the Technicon Auto Analyzer. This method is described in detail in the EPA Methods Manual. The method is applicable to surface waters and may be applicable to saline water, wastewater effluents and domestic sewage providing potential interferences are not present.

Regardless of what instrument is used, its calibration should be checked originally upon receipt and standards run each time samples are to be run in order to verify the calibration. The standards are treated in the same method except that if no organic mercury is used as the standard, the heating step can be omitted.

IV SUMMARY

The determination of the mercury content of waters has become a necessary analysis for the health of the consuming public. The method of choice has become the flameless atomic absorption procedure. Besides being simple to perform it is sensitive enough to determine the limit set for the permissible content of mercury in water.

The method can be carried out on any atomic absorption instrument that has enough physical space in its burner compartment in which to install the absorption cell. However, there are available on the market, instruments designed specifically to determine mercury via the flameless method. These instruments are generally considerably less expensive than a conventional atomic absorption spectrophotometer but have the drawback of being able to be used for only that determination.

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This outline was prepared by J. D. Pfaff, National Training Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Heavy Metals, Mercury, Water Pollution, Chemical Analysis, Metals, Spectroscopy, Spectrophotometers

DETERMINATION OF LEAD

I INTRODUCTION

Lead (Pb) is a serious cumulative body poison; it is well known for its toxicity in both acute and chronic exposures. In technologically developed countries the widespread use of lead multiplies the risk of exposure of the population to excessive levels. For this reason, constant surveillance of the lead exposure of the general population via food, air and water is necessary.

The presence of lead in water may arise from industrial, mine and smelter discharges, or from the dissolution of old lead plumbing. Tap waters which are soft, acid, and not suitably treated may contain lead resulting from an attack on the lead service pipes. Lake and river waters of the United States usually contain less than 0.05 mg/l of lead, although concentrations in excess of this have been reported. Young children present a special case in lead intoxication both in terms of tolerated intake and the severity of the symptoms. The most prevalent source of lead poisoning of children up to three years of age has been lead-containing paint still found in some older homes.

Because of the toxicity of lead to humans and because there is little information on the effectiveness of treatment processes in decreasing lead concentrations, it has been recommended that 0.05 mg/l of lead not be exceeded in public water supply sources. This number then would tend to set the limit for any analytical method which might be under consideration for use in analyzing for lead.

II METHODS

The methods used to analyze for lead are, in general, the same as those of any other heavy metal. However, there is no method for lead similar to the flameless method for mercury. The method recommended by the USEPA Methods manual is an atomic absorption method utilizing a concentration of the lead content by a chelating-extraction procedure. Other methods are available for those who are not bound to use the USEPA method.

A Dithizone

This method has been used for many years for the determination of many of the heavy metals including lead. Dithizone dissolved in carbon tetrachloride will extract lead from a slightly basic (8.5 - 9.0) solution. The lead and dithizone form a metal complex, lead dithizonate, which is soluable in carbon tetrachloride, with the formation of a red color. Measurement of the amount of red color formed yields an estimation of the lead present.

The method has sufficient sensitivity to meet the maximum contaminant level of 0.05 mg/1. Standard Methods gives the approximate minimum detection limit in water as 2 μg of Pb. The main drawback of the method is in the many operations the analyst must perform. The precision and accuracy of the method can suffer greatly due to the analyst's handling of the various operations. Analysts with long experience with the method have been able to produce acceptable results.

The procedure for the dithizone method for normal drinking waters, low in organic matter and tin, is brief and adequate. However, for industrial wastes and waters containing high organic concentrations a pretreatment step must be added. This additional step is a digestion procedure, either with a mixture of nitric and sulfuric acids or, when the organic matter is difficult to oxidize, with nitric and perchloric acids. This procedure can introduce even more error in loss of the metals during heating to dryness and is even hazardous if not followed closely.

B Other Instrumental Methods

There are other instrumental methods available even when atomic absorption is excluded. These methods would include

polarography, emission spectroscopy, neutron activation and x-ray fluorescence. Each has its own strong and weak points. Most are expensive to the point of exclusion in most laboratories but can be used to determine the concentration of lead in a sample.

C Atomic Absorption

Most metals, including lead, may be readily determined by atomic absorption spectroscopy. The method is usually simple, rapid and applicable to a large number of metals in drinking, surface and saline waters, and domestic and industrial wastes. While drinking waters may be analyzed directly, domestic and industrial wastes require processing to solubilize suspended material. Sludges and sediments and other solid type samples may also be analyzed after proper pretreatment.

Detection limits, sensitivity and optimum ranges of the metals will vary with the various makes and models of satisfactory atomic absorption spectrophotometers. The data shown in Table 1, however, provide some indication of the actual concentration ranges measurable with conventional atomization. In the majority of instances the concentration range shown in the table may be extended much lower with scale expansion and conversely extended upwards by using a less sensitive wavelength or by rotating the burner 90 degrees. Detection limits may also be extended through concentration of the sample, through solvent extraction techniques and/or the use of the so called furnace techniques. The latter includes the heated graphite atomizer, the carbon rod and the tantalum strip accessories. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. Methods of standard addition are mandatory with these furnace techniques to insure valid data.

For levels of lead below 200 μg/l, an extraction procedure is recommended. This extraction procedure is carried out at a pH of 2.8 which is the optimum pH for the extraction of lead. However, if many of the metals are to be analyzed in the same sample, either larger sample volumes must be extracted or individual extractions made for each metal being determined.

III EXTRACTION PROCEDURE

Extraction procedure with pyrrolidine dithiocarbamic acid (PDCA) in chloroform.

A Transfer 200 ml of sample into a 250 ml separatory funnel, add 2 drops bromphenol blue indicator solution and mix.

B Prepare a blank and sufficient standards in the same manner and adjust the volume of each to approximately 200 ml with deionized distilled water. All of the metals to be determined may be combined into single solutions at the appropriate concentration levels.

C Adjust the pH by addition of 2N NH_4OH solution until a blue color persists. Add HCl dropwise until the blue color just disappears; then add 2.0 ml HCl in excess. The pH at this point should be 2.3. (The pH adjustment may be made with a pH meter instead of using indicator.)

D Add 5 ml of PDCA-chloroform reagent and shake vigorously for 2 minutes. Allow the phases to separate and drain the chloroform layer into a 100 ml beaker.

E Add a second portion of 5 ml PDCA-chloroform reagent and shake vigorously for 2 minutes. Allow the phases to separate and combine the chloroform phase with that obtained in step (D).

F Determine the pH of the aqueous phase and adjust to 4.5.

G Repeat step (D) again combining the solvent extracts.

H Adjust the pH to 5.5 and extract a fourth time. Combine all extracts and evaporate to dryness on a steam bath.

TABLE 1

Atomic Absorption Concentration Ranges[1]

	Direct Aspiration					Furnace Procedure[4,5]			
Metal	Detection Limit mg/l	Sensitivity mg/l	Optimum Concentration Range mg/l			Detection Limit ug/l	Optimum Concentration Range ug/l		
Aluminum	0.1	1	5	-	50	3	20	-	200
Antimony	0.2	0.5	1	-	40	3	20	-	300
Arsenic[2]	0.002	-	0.002	-	0.02	1	5	-	100
Barium(p)	0.1	0.4	1	-	20	2	10	-	200
Beryllium	0.005	0.025	0.05	-	2	0.2	1	-	30
Cadmium	0.005	0.025	0.05	-	2	0.1	0.5	-	10
Calcium	0.01	0.08	0.2	-	7	-	-		-
Chromium	0.05	0.25	0.5	-	10	1	5	-	100
Cobalt	0.05	0.2	0.5	-	5	1	5	-	100
Copper	0.02	0.1	0.2	-	5	1	5	-	100
Gold	0.1	0.25	0.5	-	20	1	5	-	100
Iridium(p)	3	8	20	-	500	30	100	-	1500
Iron	0.03	0.12	0.3	-	5	1	5	-	100
Lead	0.1	0.5	1	-	20	1	5	-	100
Magnesium	0.001	0.007	0.02	-	0.5	-	-		-
Manganese	0.01	0.05	0.1	-	3	0.2	1	-	30
Mercury[3]	0.0002	-	0.0002	-	0.01	-	-		-
Molybdenum(p)	0.1	0.4	1	-	40	1	3	-	60
Nickel(p)	0.04	0.15	0.3	-	5	1	5	-	100
Osmium	0.3	1	2	-	100	20	50	-	500
Palladium(p)	0.1	0.25	0.5	-	15	5	20	-	400
Platinum(p)	0.2	2	5	-	75	20	100	-	2000
Potassium	0.01	0.04	0.1	-	2	-	-		
Rhenium(p)	5	15	50	-	1000	200	500	-	5000
Rhodium(p)	0.05	0.3	1	-	30	5	20	-	400
Ruthenium	0.2	0.5	1	-	50	20	100	-	2000
Selenium[2]	0.002	-	0.002	-	0.02	2	5	-	100
Silver	0.01	0.06	0.1	-	4	0.2	1	-	25
Sodium	0.002	0.015	0.03	-	1	-	-		-
Thallium	0.1	0.5	1	-	20	1	5	-	100
Tin	0.8	4	10	-	300	5	20	-	300
Titanium (p)	0.4	2	5	-	100	10	50	-	500
Vanadium (p)	0.2	0.8	2	-	100	4	10	-	200
Zinc	0.005	0.02	0.05	-	1	0.05	0.2	-	4

(1) The concentrations shown are not contrived values and should be obtainable with any satisfactory atomic absorption spectrophotometer.
(2) Gaseous hydride method.
(3) Cold vapor technique.
(4) For furnace sensitivity values consult instrument operating manual.
(5) The listed furnace values are those expected when using a 20 ul injection and normal gas flow except in the case of arsenic and selenium where gas interrupt is used. The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

I Hold the beaker at a 45 degree angle, and slowly add 2 ml of conc. distilled nitric acid, rotating the beaker to effect thorough contact of the acid with the residue.

J Place the beaker on a low temperature hotplate and evaporate just to dryness.

K Add 2 ml of nitric acid (1:1) to the beaker and heat for 1 minute. Cool, quantitatively transfer the solution to a 10 ml volumetric flask and bring to volume with distilled water. The sample is now ready for analysis.

(1)

L A second acceptable extraction procedure, the APDC-MIBK method, may be used for lead. ~~This procedure can be found in the laboratory procedure for the determination of lead in this manual.~~

IV SUMMARY

The method of choice for the determination of lead is the atomic absorption spectroscopy method. In waters that are relatively clean, such as drinking water, the lead can be determined by direct aspiration of the sample into the instrument. However, for water high in solids or having a concentration of lead below 100 μg/l the extraction procedure should be used to enhance the detection capabilities.

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This outline was prepared by J. D. Pfaff, National Training Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Lead, Metals, Water Pollution, Heavy Metals, Spectroscopy, Spectrophotometers, Chemical Analysis

NO SECTION 12 INCLUDED IN PAGINATION OR TABLE OF CONTENTS.

BORON

I SOURCES AND SIGNIFICANCE OF BORON[1][2]

A Occurrence

Boron is usually found as a sodium or calcium borate salt in nature. It is one of eight major constituents in seawater where concentrations of 4.5 mg/liter in the form of borate have been reported. It is found naturally in trace amounts in some waters or may be present from cleaning compounds and industrial waste effluents.

B Uses

Boron salts are used in leather tanning and finishing and in metallurgy, and in the production of glass, fire retardants, cosmetics, cleaning compounds, photographic materials and high energy fuels. Elemental boron can be used in nuclear reactors for neutron absorption.

C Significance

The determination of boron in waters, industrial wastes, and sewage effluents is particularly important to agriculture. Boron in small quantities is an essential element for plant growth. However, boron in excess of 2.0 mg/liter in irrigation water is harmful to most plants; some are affected by concentrations as low as 0.75 mg/liter.

There is no evidence that boron is required by animals. The ingestion of large amounts of boron can affect the central nervous system. However, drinking waters generally contain less than 0.1 mg/liter. Rarely do they contain more than 1.0 mg/liter which is still considered innocuous for human consumption.

II FEDERAL REGISTER METHODOLOGY

A NPDES

The only method recognized in the Federal Register Guidelines[3] for Analysis under the National Pollutant Discharge Elimination System is a colorimetric method using curcumin. Details of the procedure are in Standard Methods.[2]

B SDWA

Boron is not listed in the National Interim Primary Drinking Water Regulations.[4]

III SAMPLE HANDLING

A Containers

Polyethylene bottles or alkali-resistant, boron-free glassware can be used.

B Preservation

Standard Methods does not list a preservation for boron samples. In an EPA publication[5], it is suggested to include a nitric acid rinse when cleaning sample containers, and also to refrigerate samples at 4 C. It then cites a holding period of up to 6 months.

IV THE CURCUMIN METHOD[2]

A Summary

A sample of water containing boron is acidified with hydrochloric acid and evaporated in the presence of curcumin. The reaction forms a red-colored product called rosocyanine. The rosocyanine is taken up in ethyl alcohol and the red color in the solution is compared to that of standards in a spectrophotometer at a wavelength of 540 nm.

B The Curcumin Reagent

1. The chemicals are added to the sample in a single addition of a combined curcumin reagent. This contains curcumin, the color reagent; oxalic acid which serves to intensify the

color; and concentrated hydrochloric acid to control pH. Ethyl or isopropyl alcohol is the solvent because the product of the reaction, rosocyanine, is soluble in alcohol.

2. There are at least two interpretations of the curcumin reaction[6] as shown in Figures 1 and 2. If Figure 1 is the correct interpretation, more curcumin is required. Thus, the combined reagent is prepared and measured to maintain an excess for either reaction as long as the boron concentration is within the stated scope of the test.

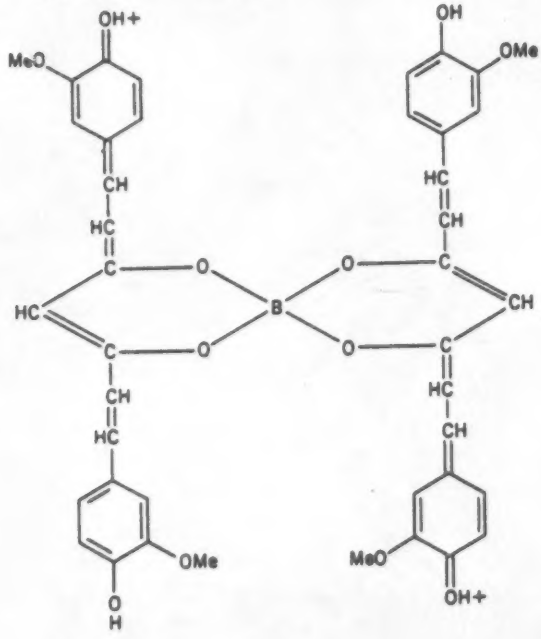


Figure 1
Curcumin-Rosocyanine Reaction
One View

C Scope and Application

The optimum range of the test is 0.1 to 1.0 mg/liter boron. This range can be extended by dilution. The method is applicable to drinking and surface waters, domestic and industrial wastes.

D Pretreatment of Samples

The Federal Register Guidelines do not specify any pretreatment such as digestion for determining total boron. To determine dissolved boron, the filtrate obtained from filtration through a 0.45 μm membrane filter is to be used.

E Interferences

1. Hardness Cations

Calcium, magnesium and other cations interfere with the spectrophotometric measurements. These form salts which will not dissolve in ethyl alcohol, thereby contributing turbidity to the solution of rosocyanine. Such cationic interferences can be removed in two ways.

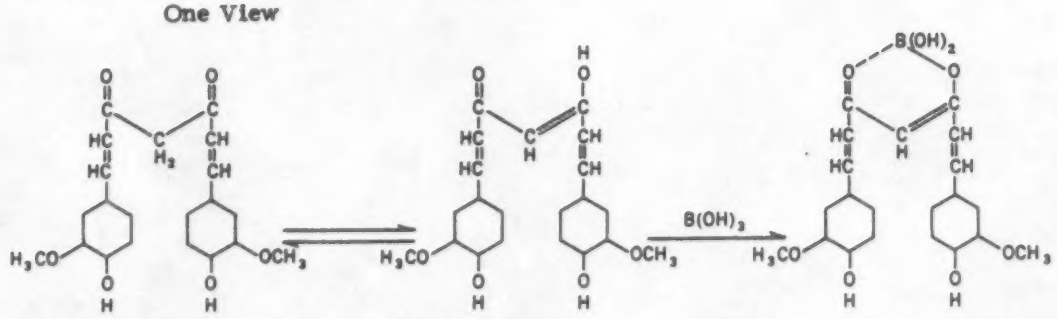


Figure 2
Curcumin-Rosocyanine Reaction
Another View

a. For hardness content greater than 100 mg/liter $CaCO_3$, the sample can be passed through a column of strongly acidic cation - exchange resin in the hydrogen form to remove the interfering cations prior to the determination.

b. For smaller quantities, filter the samples after rosocyanine is formed and dissolved in the alcohol.

2. Nitrate Nitrogen

Nitrate nitrogen concentrations above 20 mg/liter interfere.

F Variables to be Controlled

1. Volumes and Concentrations

Small volumes (less than 1.0 ml) are involved in the analysis. Also, the alcohol solvent has low viscosity. Skillful pipeting is required. Also, reagents must be very accurately prepared.

2. Evaporation Time

a. To insure equal time, evaporating dishes must be identical in shape, size and composition.

b. Since the time of evaporation affects the intensity of color, the procedure suggests a standard eighty minute period for this step.

3. Temperature

The procedure specifies a water bath set at 55 $\pm$ 2 C.

V ACCURACY AND PRECISION

A synthetic unknown sample prepared by the Analytical Reference Service, PHS, containing 240 μg/liter B, 40 μg/liter As, 250 μg/liter Be, 20 μg/liter Se and 6 μg/liter V in distilled water was analyzed in 30 laboratories by the curcumin method. Relative standard deviation was 22.8%. Relative error was 0%.

REFERENCES

1. . Quality Criteria for Water, 1976, U.S. EPA, Government Printing Office No. 1977-0-222-904, Washington, D.C.

2. Standard Methods for the Examination of Water and Wastewater, 14th ed., 1975, APHA, Washington, D.C., 20036.

3. Federal Register, Vol. 41, No. 232, Wednesday, December 1, 1976, Title 40, Chapter 1, Subchapter D, Part 136, page 52780.

4. Federal Register, Vol. 40, No. 248, Wednesday, December 24, 1975, Title 40, Chapter 1, Subchapter D, Part 141, page 59566.

5. Handbook for Sampling and Sample Preservation of Water and Wastewater, EPA-600/4-76-049, EMSL, ORD, U.S. EPA, Cincinnati, Ohio 45268.

6. Lishka, R.J., Comparison of Analytical Procedures for Boron JAWWA. Vol. 53, No. 12. December, 1961.

This outline was prepared by A.D. Kroner, Chemist, National Training and Operational Technology Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Boron, Metals, Chemical Analysis, Water Analysis, Irrigation Effects

LABORATORY PROCEDURE FOR BORON, CURCUMIN METHOD

I SOURCE OF PROCEDURE

This procedure is from Standard Methods[1]. The one difference presented here is an increase in the concentration of the standard boron solution and a related increase in volumes when preparing the calibration standards. The change was made to minimize errors in the test that could occur because such small volume measurements (less than 1.0 ml) would otherwise be required. This does not constitute a variance in the methodology.

II APPLICABILITY

The test is applicable to concentrations of boron from 0.1 to 1.0 mg/litre. The range can be extended by dilution. It can be used for drinking and surface waters, domestic and industrial wastes.

III REAGENTS

Note: For storage of reagents it is preferable to use polyethylene, alkali-resistant glassware, or vessels made of ordinary soft glass. Borosilicate glassware should be avoided for storage vessels.

A Stock Boron Solution

Dissolve 571.6 mg anhydrous boric acid, H_3BO_3, in distilled water and dilute to 1,000 ml; 1.00 ml = 100 µg B. Because H_3BO_3 loses weight on drying at 105 C, use a reagent meeting ACS specifications and keep the bottle tightly stoppered to prevent the entrance of atomspheric moisture.

B Standard Boron Solution

On the day of use, dilute 100.0 ml of stock boron solution to 1000 ml with distilled water. 1.00 ml = 10 µg B.

Note: This is 10 times the concentration cited in Standard Methods. The change was made to avoid later measurements of less than 1.0 ml volumes.

C Curcumin Reagent

Dissolve 40 mg finely ground curcumin and 5.0 g oxalic acid in 80 ml of 95% ethyl alcohol contained in a 100 ml volumetric flask. Add 4.2 ml conc HCl and make the solution up to 100 ml with ethyl alcohol (isopropyl alcohol, 95%, may be used in place of ethyl alcohol). This reagent will be stable for several days if stored in a refrigerator.

D Alcohol

Ethyl or isopropyl alcohol, 95%.

IV EQUIPMENT PREPARATIONS

A Evaporating dishes identical in shape, size and composition. Dishes should be clean and free of scratches.

B Water Bath, checked and heated to a temperature of 55 ± 2 C of a size to accomodate 5 evaporating dishes for standards plus evaporating dishes for the samples to be run.

C Spectrophotometer checked for accurate operation at 540 nm, with a minimum light path of 1 cm and warmed up for operation.

V ANALYTICAL PROCEDURE

A Preparation of Calibration Standards

Note: A calibration curve should be prepared each day the test is run. If the curve has been established, prepare a blank and the 0.50 mg/litre standard to run with samples as a check on the validity of the standard curve.

1. On the data sheet, record the date and time analysis begins.

2. Label four 100 ml volumetric flasks respectively as 0.20, 0.50, 0.80 and 1.00 mg/litre boron. A fifth container for the distilled water blank (0.00 mg/litre boron) will also be required.

3. Pipet into each flask the corresponding ml of standard boron solution as shown in this table:

Boron, mg per liter	Boron, ml Standard
0.00	None
0.20	2
0.50	5
0.80	8
1.00	10

4. Put about 40 ml of distilled water in the flask for the blank, 0.00.

5. Use distilled water to bring the volume to 100.0 ml in the flasks containing standard boron solution.

6. Stopper the flasks and mix well by inverting.

B Color Development

1. Mark five identical 100 ml evaporating dishes with the boron concentrations shown in the table above (A. 3.).

2. Use clean, dry volumetric pipets (5) to measure 1.0 ml of the blank and of each standard into an evaporating dish labeled with the corresponding boron concentration.

3. Record sample identification information on the data sheet.

4. Mark evaporating dishes identical to those used for the standards with codes for the samples to be run.

5. Use a clean, dry volumetric pipet for each sample to measure 1.0 ml into the evaporating dish labeled with a code for that sample. (If analysis has shown that a sample is beyond the 1.0 mg/litre boron limit of the test, the sample must be diluted so 1.0 ml of the diluted sample does fall in that test limit. Record the volumes if you dilute.)

6. Use a volumetric pipet (for control) to add 4.0 ml curcumin reagent to the solution in each evaporating dish.

7. Gently swirl each dish.

8. Float the dishes on a water bath at 55 $\pm$ 2 C and let them remain for 80 minutes. This is usually sufficient for complete drying and removal of HCl. Keep the drying time constant for standards and samples.

9. Remove the dishes from the water bath, being careful that water from the bottom of dishes does not drop into other dishes still in the bath.

10. Record the time because all spectrophotometric readings must be done within one hour from now.

11. Allow the dishes to cool to room temperature.

C Dissolving the Residue

1. For each sample, mark a 25 ml volumtric flask with the corresponding sample code.

2. The contents of the evaporating dish with the same code must be dissolved and transferred quantitatively to the labeled 25 ml flask. Use at least 3 small quantities of alcohol to do this. To dislodge and stir the residue into solution, use a polyethylene rod. A medicine dropper works well for the actual transfer. The dropper should get a final alcohol rinse into the flask. Use very small volumes of alcohol because 25 ml is the final desired volume.

3. Using alcohol, bring the volume in the flask to 25.0 ml. Stopper the flask and mix well by inverting.

4. If the solution appears turbid, start the filtration procedure described in D below. While the sample is filtering, dissolve and transfer the contents of the remaining evaporating dishes into appropriately-labeled 25 ml volumetric flasks using the directions in steps 2 and 3 above. You have one hour to complete any filtrations and transfers to the 25 ml volumetric flasks and to take all the absorbance readings (E).

D Filtration of Turbid Samples

1. Mark a very small beaker with the sample identification code.

2. Set up a filtration assembly consisting of a clay triangle on a small ring connected to a stand and a small funnel with a fitted piece of Whatman No. 30 or equivalent filter paper. Do not "wet" the filter paper.

3. Using a small glass rod, transfer portions of the 25.0 ml of sample from the flask to the filter paper.

4. Do not rinse the flask. The sample has already been measured at 25 ml. A quantitative transfer is not necessary at this stage. You only need about 15 ml for the spectrophotometric reading which is the next procedure.

E Spectrophotometric Readings

1. The instrument should be warmed up and set at a wavelength of 540 nm.

2. Set the instrument at infinite absorbance.

3. Use the blank (0.00 mg/litre boron) to set the instrument at zero absorbance.

4. Remove the blank and check if the scale reading returns to infinite absorbance. If it doesn't, repeat steps 2, 3 and this step until the spectrophotometer checks out.

5. Record the time on the data sheet to verify that the readings are being taken within one hour of the end of the evaporation step.

6. Read and record the absorbances of the standards and of the samples on the data sheet. Use alcohol to rinse out the cell after each use.

F Calibration Curve

1. Plot the absorbances for the four calibration standards against their concentrations on an appropriately-labeled arithmetic graph.

2. Draw the best-fit straight line along the points and through zero to produce a calibration curve.

3. For each sample, use its absorbance reading and the calibration curve to find its concentration. If the sample was diluted prior to analysis, record and apply the appropriate dilution factor to the curve concentration to obtain the final result. Sign the data sheet.

4. It is often convenient to express final results as µg/litre boron.

REFERENCE

1. Standard Methods for the Examination of Water and Wastewater, 14th ed., 1975, APHA, Washington, D.C., p. 287.

This outline was prepared by A.D. Kroner, Chemist, National Training and Operational Technology Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Boron, Analytical Techniques, Chemical Analysis, Laboratory Tests, Water Analysis, Metals

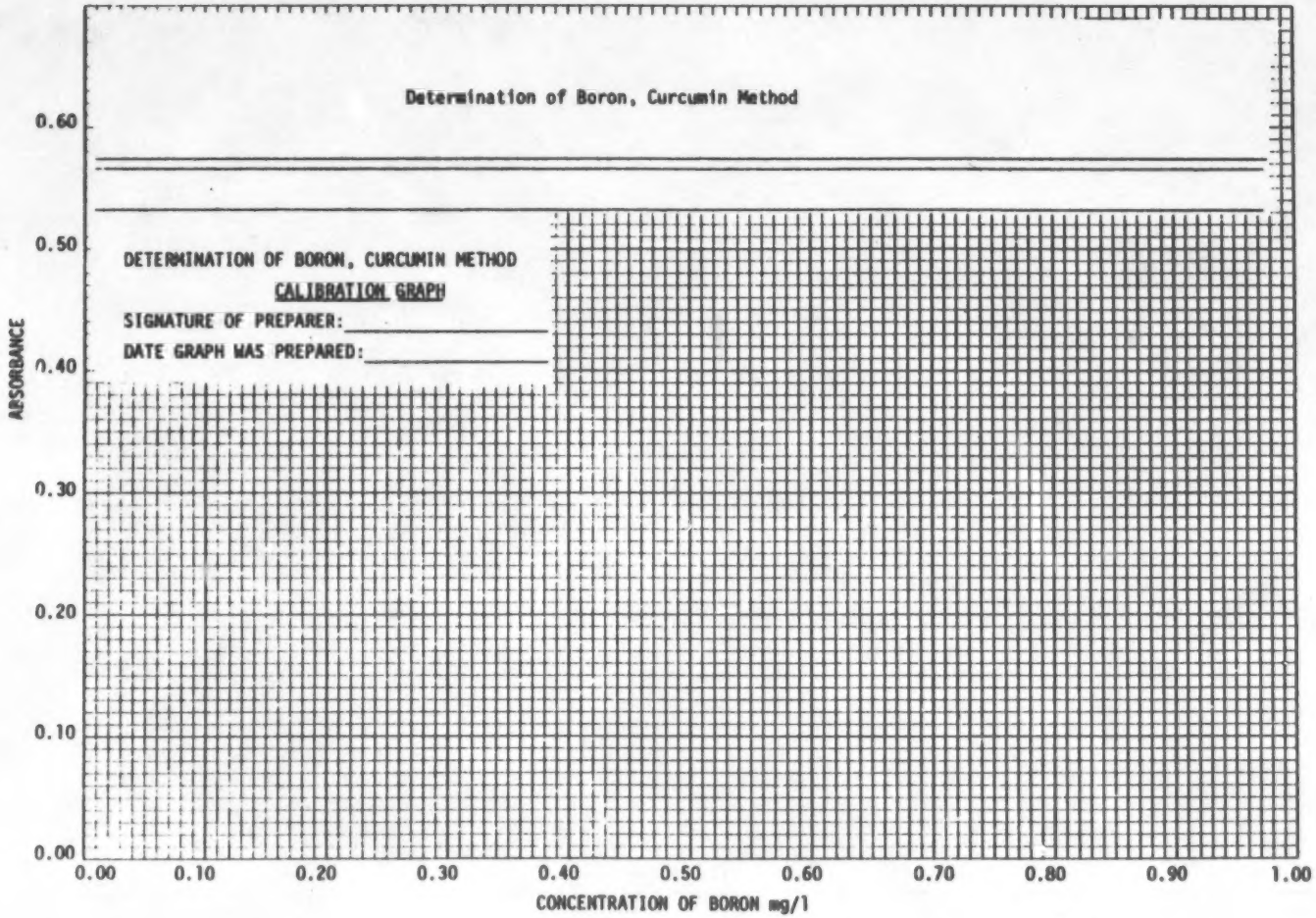
BORON CURCUMIN METHOD

EMPLOYER _____

Item		Sample	Sample	Sample	Standards
1	Identification Code				
2	Type (grab or composite)				
3	Date and Time Collected				
4	Sample Collector				
5	Date and Time Analysis Began				
6	Dilution Volumes				
7	Time Evaporation Ended				
8	Time Absorbances Read				
9	Comments				

ABSORBANCES AND RESULTS

	Identification	Absorbance	Dilution Factor	Final mg/l B
10	0.00 mg/l B			
	0.20 mg/l B			
	0.50 mg/l B			
	0.80 mg/l B			
	1.00 mg/l B			
11	Sample #			
	Sample #			
	Sample #			
	Sample #			
12	Analyst			


Determination of Boron, Curcumin Method
DETERMINATION OF BORON, CURCUMIN METHOD
CALIBRATION GRAPH
SIGNATURE OF PREPARER:
DATE GRAPH WAS PREPARED:
ABSORBANCE
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
CONCENTRATION OF BORON mg/l